Through the Probe Auditing of Ambient Air Monitoring Instruments at Trace Levels:

Part I: Current Capabilities

Part II: Evaluation and Comparison of an Alternative Method

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Requirements, Needs, and Authority For Trace Level Auditing
NCore

Technology Transfer Network
Ambient Monitoring Technology Information Center

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NCore Multipollutant Monitoring Network

NCore is a multi pollutant network that integrates several advanced measurement systems for particles, pollutant gases and meteorology. Most NC
start of the network on January 1, 2011.

Monitoring Objectives

The NCore Network addresses the following objectives:

- Timely reporting of data to public by supporting AIRNow, air quality forecasting, and other public reporting mechanisms;
- Support for development of emission strategies through air quality model evaluation and other observational methods;
- Accountability of emission strategy progress through tracking long-term trends of criteria and non-criteria pollutants and their precursors;
- Support for long-term health assessments that contribute to ongoing reviews of the NAAQS;
- Compliance through establishing nonattainment/attainment areas through comparison with the NAAQS;
- Support to scientific studies ranging across technological, health, and atmospheric process disciplines; and
- Support to ecosystem assessments recognizing that national air quality networks benefit ecosystem assessments and, in turn, benefit from

Measurements

Requirements, Needs, and Authority For Trace Level Auditing
NCore

Measurements

Parameter	**Comments**
PM2.5 speciation	Organic and elemental carbon, major ions and trace metals (24 hour average; every 3rd day); IMPROVE or CSN
PM2.5 FRM mass	24 hr. average at least every 3rd day
continuous PM2.5 mass	1 hour reporting interval; FEM or pre-FEM monitors
PM(10-2.5) mass	Filter-based or continuous
ozone (O3)	all gases through continuous monitors
carbon monoxide (CO)	capable of trace levels (low ppm and below) where needed
sulfur dioxide (SO2)	capable of trace levels (low ppb and below) where needed
nitrogen oxide (NO)	capable of trace levels (low ppb and below) where needed
total reactive nitrogen (NOy)	capable of trace levels (low ppb and below) where needed
surface meteorology	wind speed and direction (reported as "Resultant"), temperature, RH

Requirements, Needs, and Authority For Trace Level Auditing

40 CFR Part 58 Appendix A

ELECTRONIC CODE OF FEDERAL REGULATIONS

e-CFR Data is current as of July 30, 2014

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Title 40: Protection of Environment
PART 58—AMBIENT AIR QUALITY SURVEILLANCE
Subpart G—Federal Monitoring

APPENDIX A TO PART 58—QUALITY ASSURANCE REQUIREMENTS FOR SLAMS, SPMS AND PSD AIR MONITORING

1. General Information
2. Quality System Requirements
3. Measurement Quality Check Requirements
4. Calculations for Data Quality Assessments
5. Reporting Requirements
6. References

Requirements, Needs, and Authority For Trace Level Auditing

40 CFR Part 58 Appendix A

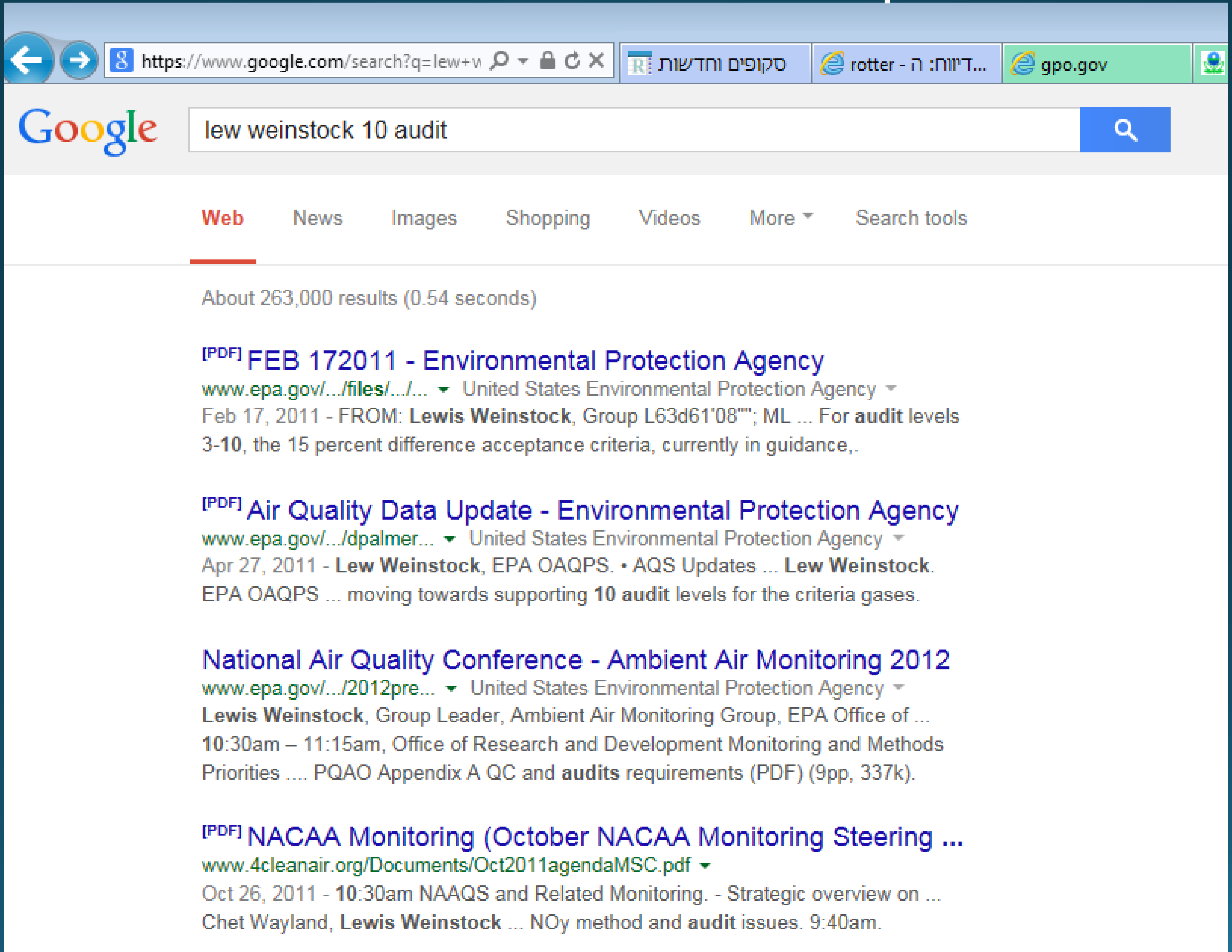
3.2.2.1 (a) The evaluation is made by challenging the analyzer with audit gas standard of known concentration (effective concentration for open path analyzers) from at least three consecutive audit levels. The audit levels selected should represent or bracket 80 percent of ambient concentrations measured by the analyzer being evaluated:

Audit level	Concentration range, ppm			
	O_3	SO_2	NO_2	CO
1	0.02-0.05	0.0003-0.005	0.0002-0.002	0.08-0.10
2	0.06-0.10	0.006-0.01	0.003-0.005	0.50-1.00
3	0.11-0.20	0.02-0.10	0.006-0.10	1.50-4.00
4	0.21-0.30	0.11-0.40	0.11-0.30	5-15
5	0.31-0.90	0.41-0.90	0.31-0.60	20-50

(b) An additional 4th level is encouraged for those monitors that have the potential for exceeding the concentration ranges described by the initial three selected.

Requirements, Needs, and Authority For Trace Level Auditing

OAQPS Memo On 10 Audit Levels & Acceptance Criteria



Requirements, Needs, and Authority For Trace Level Auditing

OAQPS Memo On 10 Audit Levels & Acceptance Criteria

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

FEB 17 2011

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

MEMORANDUM

SUBJECT: Guidance on Statistics for Use at Audit Levels 1 and 2 of the Expanded List of Audit Levels for Annual Performance Evaluation for SO_2, NO_2, O_3, and CO as Described in 40 CFR Part 58 Appendix A Section 3.2.2

FROM: Lewis Weinstock, Group Leader
Mike Papp, QA Team Lead
Ambient Air Monitoring Group (C304-06)

TO: Air Monitoring Program Managers and Staff

On November 18, 2010, a technical memorandum[1] that allowed for the expansion of the performance evaluation audit levels from five (currently in CFR) to ten was distributed. The expansion allowed EPA to provide lower audit levels for use at NCore sites or sites reporting low routine concentrations and tightened up the span within each level to provide more choices of ranges where routine concentrations are being measured.

We have received comment from monitoring organizations and EPA Regions expressing concerns that the lower audit ranges will create large, unreasonable percent differences (PDs) if the same statistics and current acceptance limits are used. They are suggesting that EPA look to a different statistic at these lower audit ranges.

Using 1-point QC check data and annual performance evaluation data in AQS, recent NPAP through-the-probe data at NCore sites and some low concentration calibration information from our RTP Ambient Air Innovation Research Station (AIRS), EPA evaluated the effect of low-level concentrations against our current PD statistic. Attachment 1 provides the results of this evaluation.

[1] Expanded List of Audit Levels for Annual Performance Evaluation for SO_2, NO_2, O_3, and CO as Described in 40 CFR Part 58 Appendix A Section 3.2.2 http://www.epa.gov/ttn/amtic/cpreldoc.html

Requirements, Needs, and Authority For Trace Level Auditing

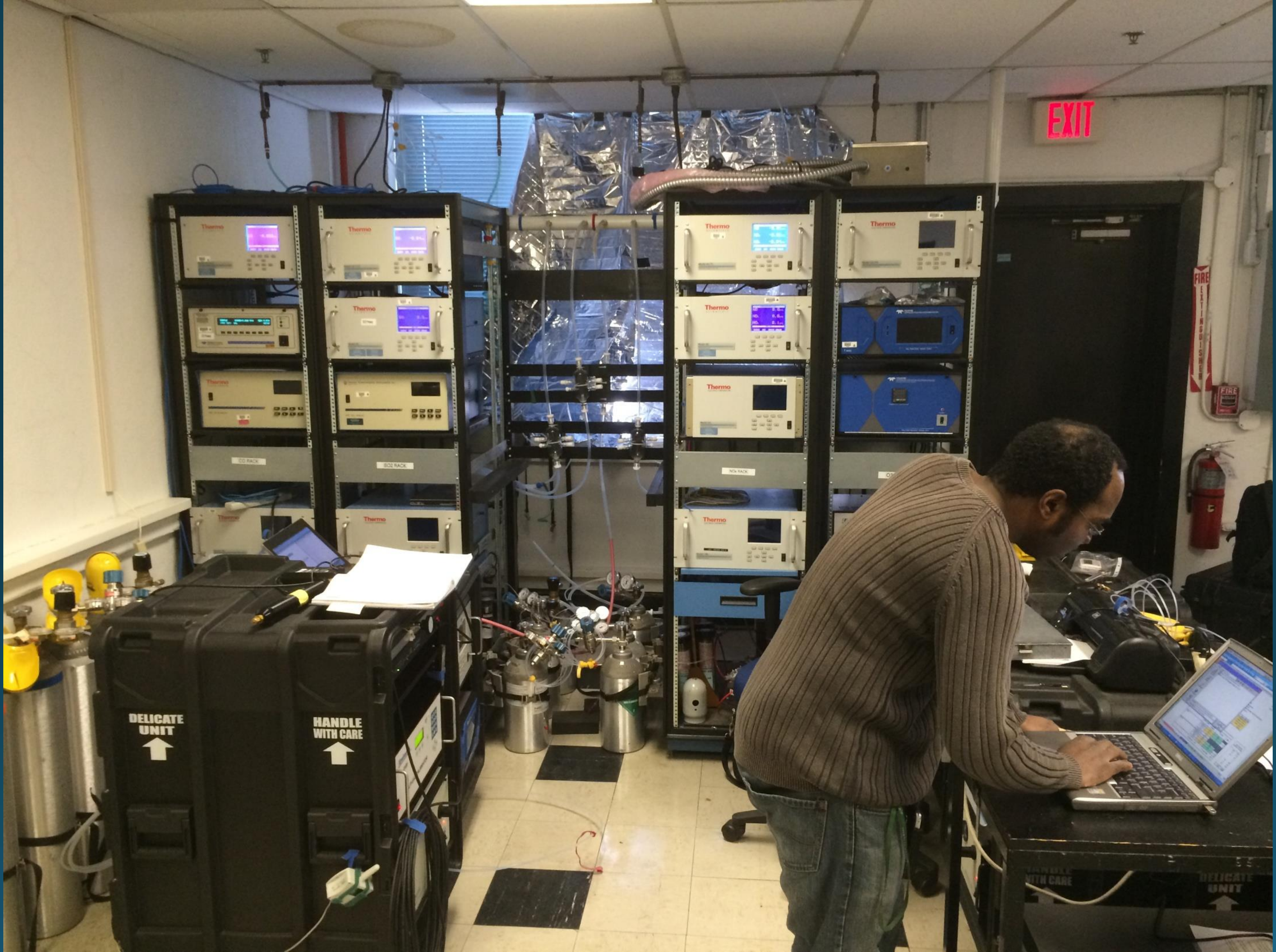
OAQPS Memo On 10 Audit Levels & Acceptance Criteria - Summarized

EPA Ambient Air Audit Levels				
	Concentration in ppb			Conc. In ppm
Level	**O3**	**SO2**	**NO2**	**CO**
1	4-5.9	0.3-2.9	0.3-2.9	0.02-0.059
2	6-19	3-4.9	3-4.9	0.06-0.199
3	20-39	5-7.9	5-7.9	0.20-0.899
4	40-69	8-19.9	8-19.9	0.9-2.999
5	70-89	20-49.9	20-49.9	3-7.999
6	90-119	50-99.9	50-99.9	8-15.999
7	120-139	100-149.9	100-149.9	16-30.999
8	140-169	150-259.9	150-259.9	31-39.999
9	170-189	260-799.9	260-799.9	40-49.999
10	190-259	800-1000	800-1000	50-60
Audit Limits for SO2 & NO2 are ±15% and @ Levels 1 and 2 ±0.0015 ppb				
Audit Limits for CO are ±15% and @ Levels 1 and 2 ±0.03 ppm				

Materials

- Trace Through The Probe (TTP) auditing system consisting of:
  - Zero Air Supply
  - Trace CO Analyzer w/Zero, Span & Precision Gas Standards (0, 4.14, & 0.741 ppm CO)
  - Gas Phase Titration Calibrator (GPT), w/ Calibrated Mass Flow Controllers
  - Multi-blend audit gas (CO/SO2/NOx @454/15.23/29.68 ppm)
- Laboratory:
  - Racks w/ Trace CO, SO2, and NOx analyzers
  - NIST SRM Calibration Standards for CO, SO2, NOx
  - Primary Flow Standards for at 1-30 L/min, 5-300 cc/min, and 0.5-50 cc/min
- Field:
  - Ncore Monitoring Stations in NY State: Rochester, Pinnacle State Park, Queens College
  - Ncore Monitoring Station in NJ: Newark


FURMAN
Environics
6100
MULTI-GAS CALIBRATOR
Thermo
ELECTRON CORPORATION
Model 49i-PS
TELEDYNE
ADVANCED POLLUTION INSTRUMENTATION
CO 0.003 PPM
T SERIES


EXIT
DELICATE UNIT
HANDLE WITH CARE


Thermo


Thermo
Thermo

Procedure – Air Lab Tests

Air Lab tests were conducted on 7 separate days. On each day:

1. Calibration of lab CO, SO_2, & NO_x trace analyzers w/ NIST SRMs at the following ranges:
   - CO: 0 - 5.0 ppm
   - SO_2: 0 - 100 ppb
   - NO_x: 0 - 200 ppb

Procedure – Air Lab Tests

2. R2 TTP audit of lab analyzers as follows:

- Calibration of TTP CO analyzer by undiluted zero & span gas standards, followed by sampling undiluted precision gas standard.
- Audit of lab NOx, SO_2, and CO analyzers, at levels 5 through 1, using the TTP multi gas blend and GPT calibrator. The TTP CO analyzer samples the same gas stream as the audited instruments.
- Post audit sampling of undiluted zero, span & precision gas standards by the TTP CO analyzer.
- Linear regression run on TTP CO analyzer response to pre & post audit zero, span, and precision gas standards.
- TTP CO analyzer audit response is corrected using the regression curve.
- "True" CO audit concentrations are determined directly from corrected CO analyzer results; "True" SO_2 and NOx audit concentrations are determined by:

  [corrected CO results] * [proportion of SO_2 or NOx relative to CO in multi-blend audit gas]
- A separate set of audit results, based on calibration of the GPT mass flow controllers, are also collected

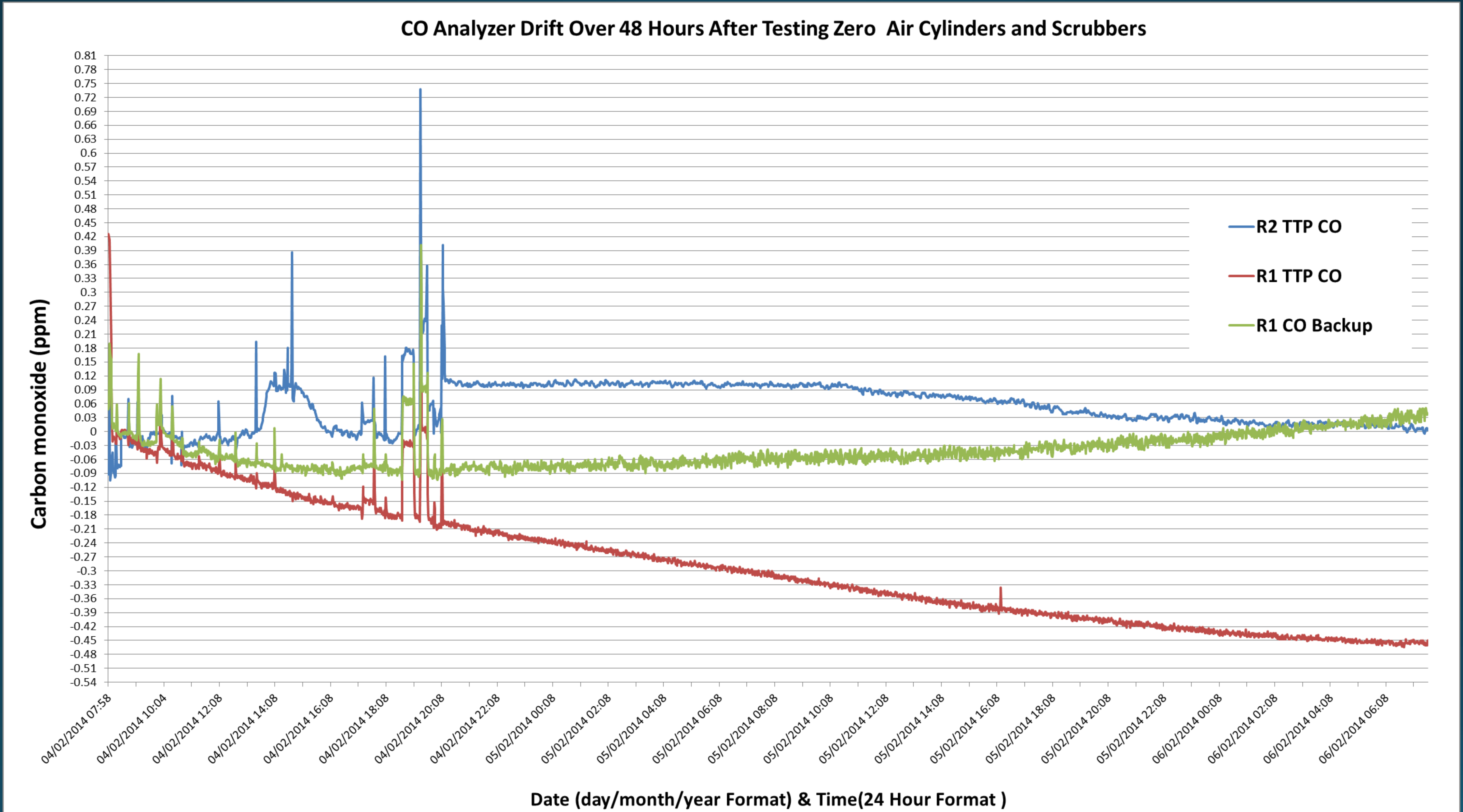
Limitations

TTP CO analyzer based systems have proven reliable and accurate at concentrations from 7-50 ppm CO.

At trace concentrations (<0.5 ppm CO), there are significant vulnerabilities with respect to:

- Drift and drift corrections
- Interference due to humidity, CO_2, or other hydrocarbons
- Calibration gas accuracy and purity

Drift



CO Analyzer Drift Over 48 Hours After Testing Zero Air Cylinders and Scrubbers
Carbon monoxide (ppm)
0.81
0.78
0.75
0.72
0.69
0.66
0.63
0.6
0.57
0.54
0.51
0.48
0.45
0.42
0.39
0.36
0.33
0.3
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
0
-0.03
-0.06
-0.09
-0.12
-0.15
-0.18
-0.21
-0.24
-0.27
-0.3
-0.33
-0.36
-0.39
-0.42
-0.45
-0.48
-0.51
-0.54
R2 TTP CO
R1 TTP CO
R1 CO Backup
04/02/2014 07:58
04/02/2014 10:04
04/02/2014 12:08
04/02/2014 14:08
04/02/2014 16:08
04/02/2014 18:08
04/02/2014 20:08
04/02/2014 22:08
05/02/2014 00:08
05/02/2014 02:08
05/02/2014 04:08
05/02/2014 06:08
05/02/2014 08:08
05/02/2014 10:08
05/02/2014 12:08
05/02/2014 14:08
05/02/2014 16:08
05/02/2014 18:08
05/02/2014 20:08
05/02/2014 22:08
06/02/2014 00:08
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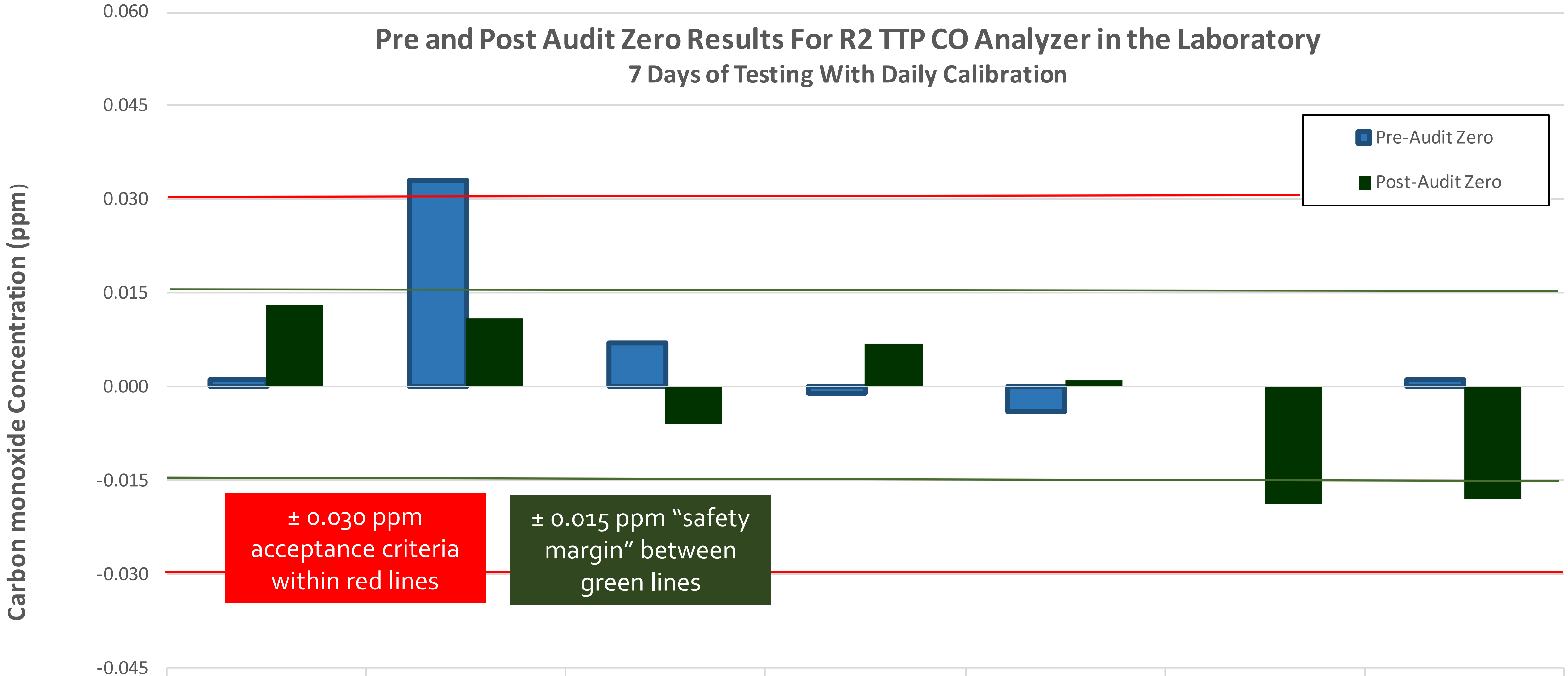
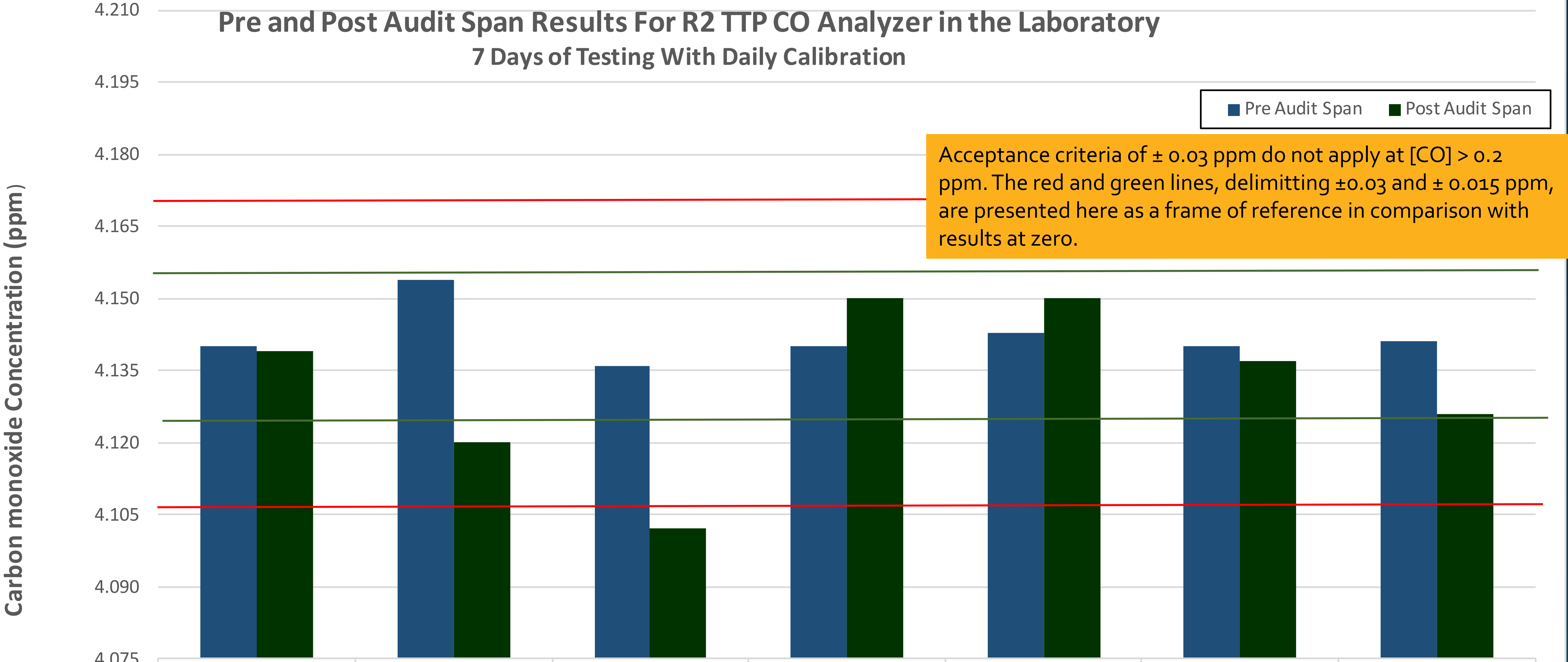
06/02/2014 06:08
Date (day/month/year Format) & Time(24 Hour Format)

Drift



	Day 1 - Air lab	Day 2- Air lab	Day 3 - Air lab	Day 4 - Air lab	Day 5 - Air lab	R3-R2 Comp	R1-R2 Comp
Pre-Audit Zero	0.001	0.033	0.007	-0.001	-0.004	0.000	0.001
Post-Audit Zero	0.013	0.011	-0.006	0.007	0.001	-0.019	-0.018

Drift



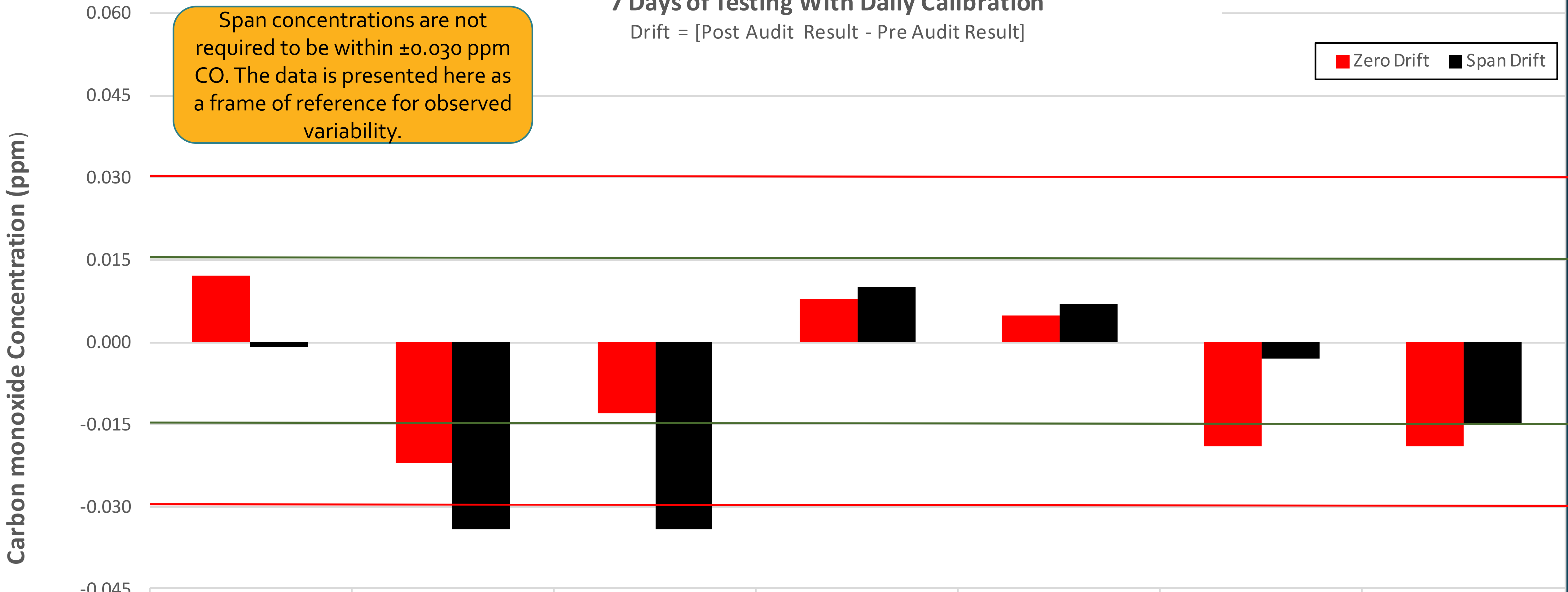
	Day 1 - Air lab	Day 2- Air lab	Day 3 - Air lab	Day 4 - Air lab	Day 5 - Air lab	R3-R2 Comp	R1-R2 Comp
Pre Audit Span	4.140	4.154	4.136	4.140	4.143	4.140	4.141
Post Audit Span	4.139	4.120	4.102	4.150	4.150	4.137	4.126

Drift

Zero and Span Drift for R2 TTP CO Analyzer in the Laboratory

7 Days of Testing With Daily Calibration

Drift = [Post Audit Result - Pre Audit Result]



	Day 1 - Air lab	Day 2- Air lab	Day 3 - Air lab	Day 4 - Air lab	Day 5 - Air lab	R3-R2 Comp	R1-R2 Comp
Zero Drift	0.012	-0.022	-0.013	0.008	0.005	-0.019	-0.019
Span Drift	-0.001	-0.034	-0.034	0.010	0.007	-0.003	-0.015

Finding #1:

Zero drift for the R2 TTP CO analyzer was within ±0.03 ppm CO.

Finding #2:

Zero & span drifted in the same direction and were ± 0.03 ppm of each other on 6 of 7 days.

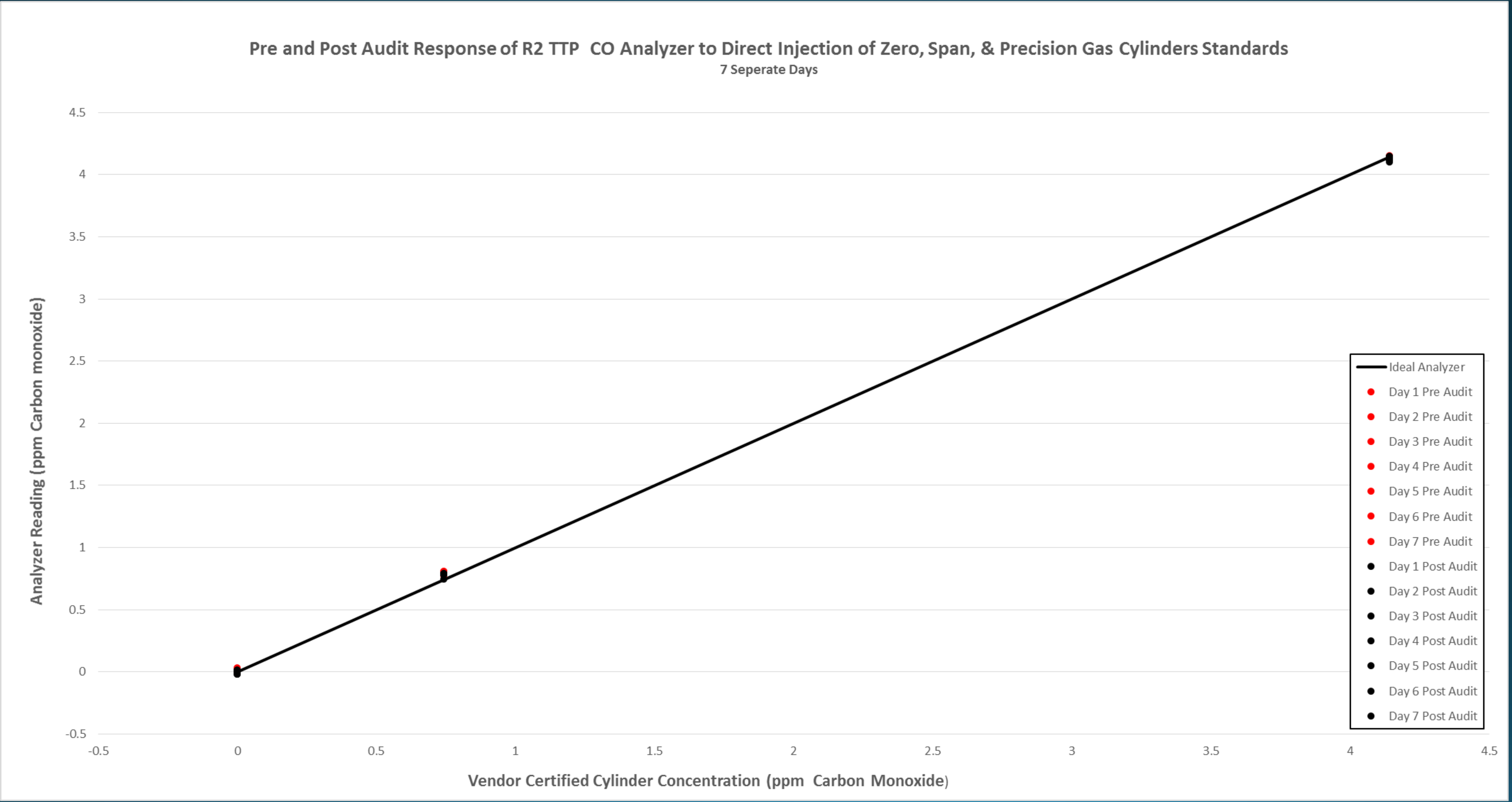
Implication

Post audit CO span sample may be eliminated, as span drift can be corrected by zero drift assessment alone.

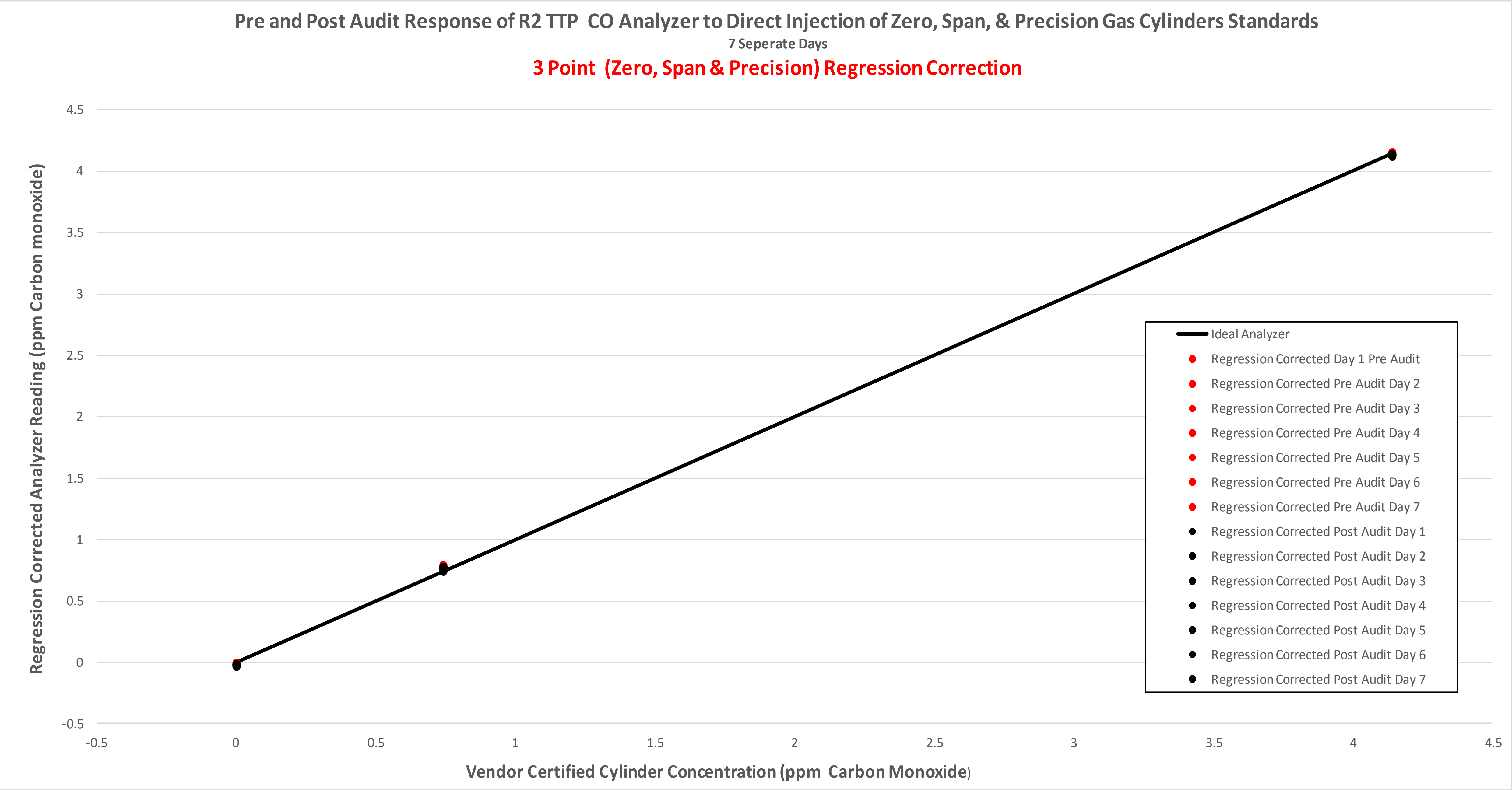
Regression Correction for Drift

- By the original TTP method, correction for drift is done by linear regression, using undiluted gas standards pre and post audit, @ the following concentrations:
  - 4.140 ppm CO (span),
  - 0.741 ppm CO (precision)
  - Zero
- Regression correction assumes:
  - The analyzer response is linear
  - Three points (span, precision, and zero) provides sufficient resolution to calibrate the CO analyzer response
  - The gas standard concentrations are accurate

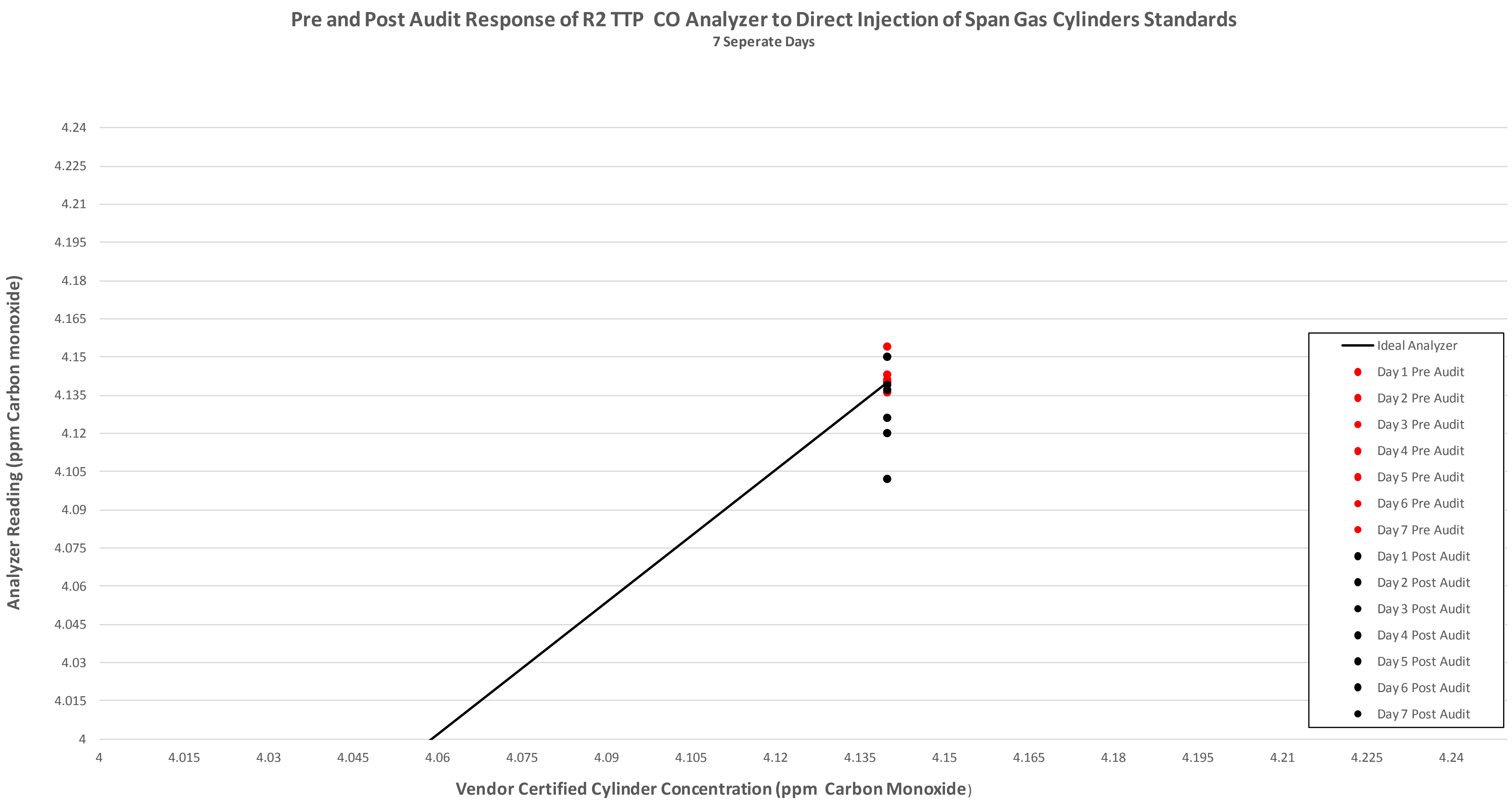
No Regression Correction for Drift – Full Curve



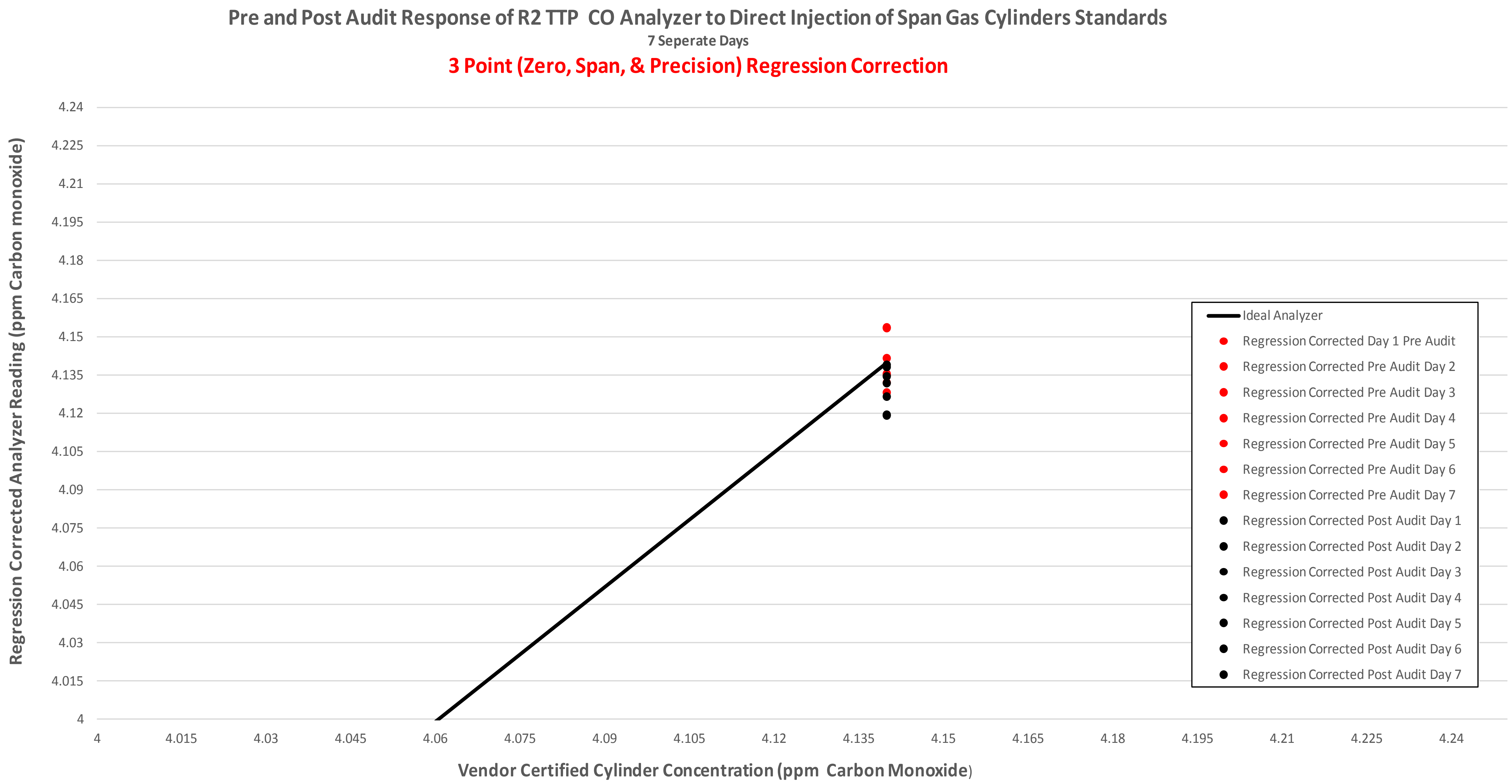
3 Point Regression Correction for Drift – Full Curve



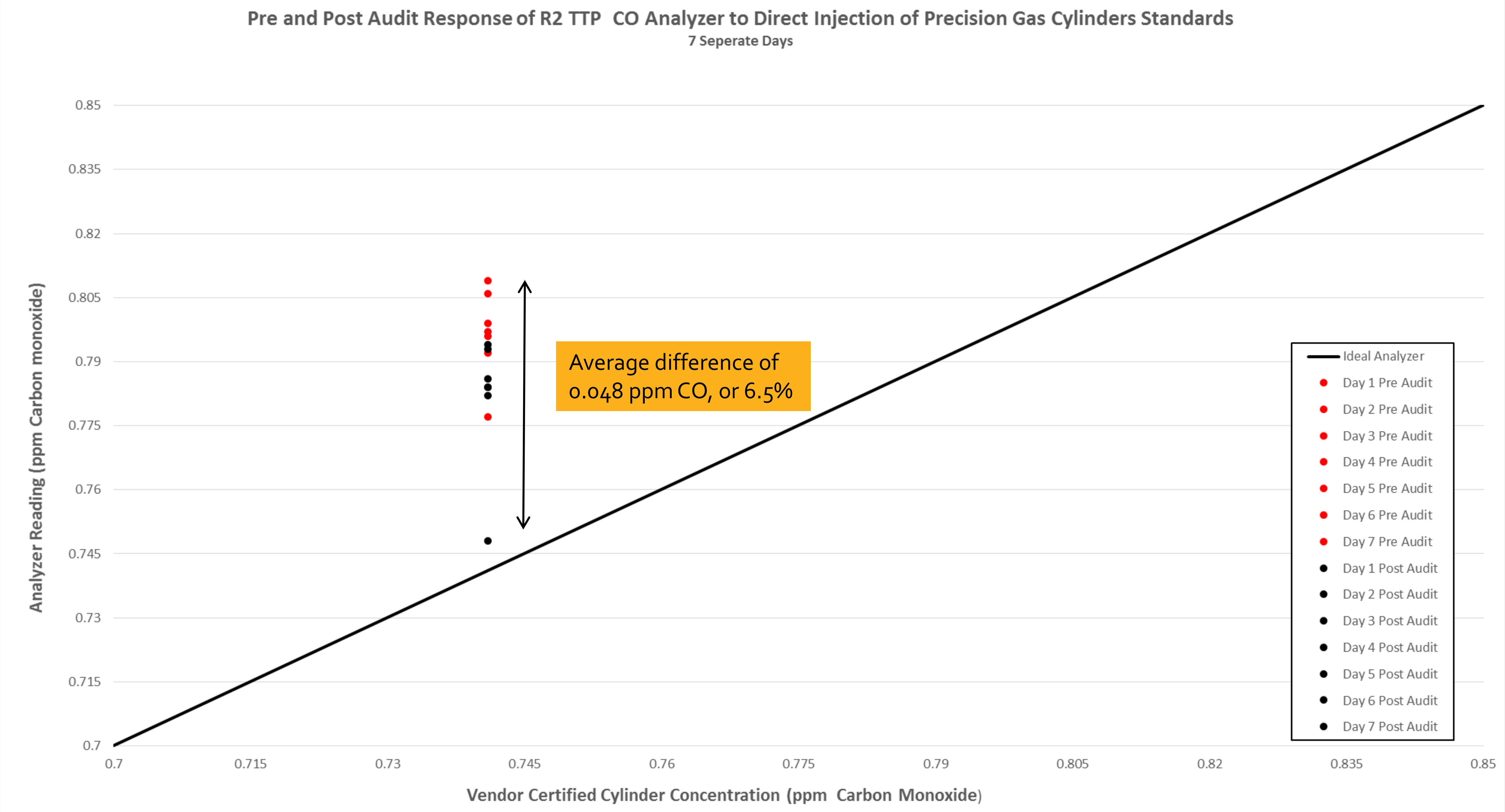
No Regression Correction for Drift - Span Point Close Up



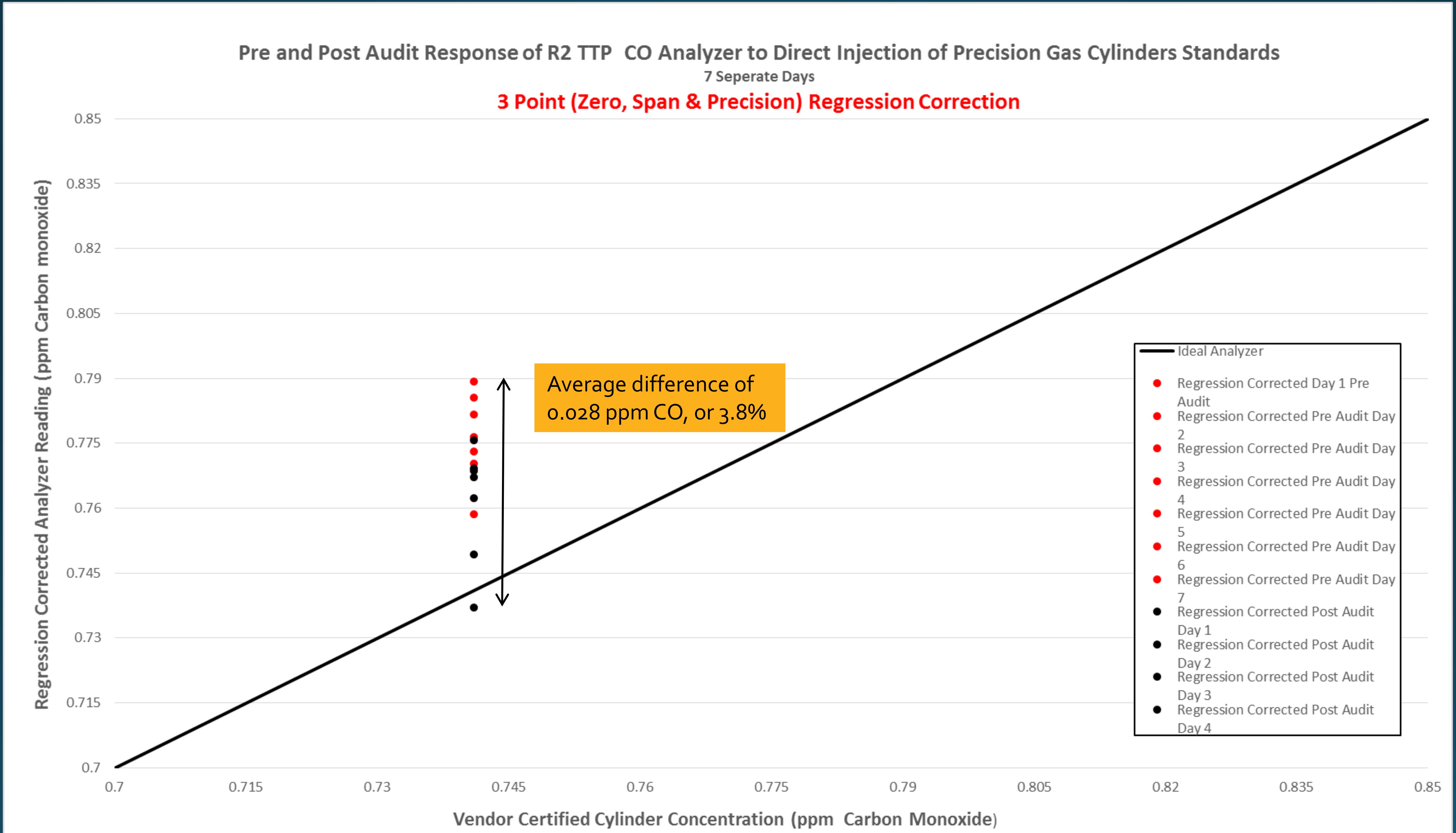
3 Point Regression Correction for Drift – Span Point Close Up



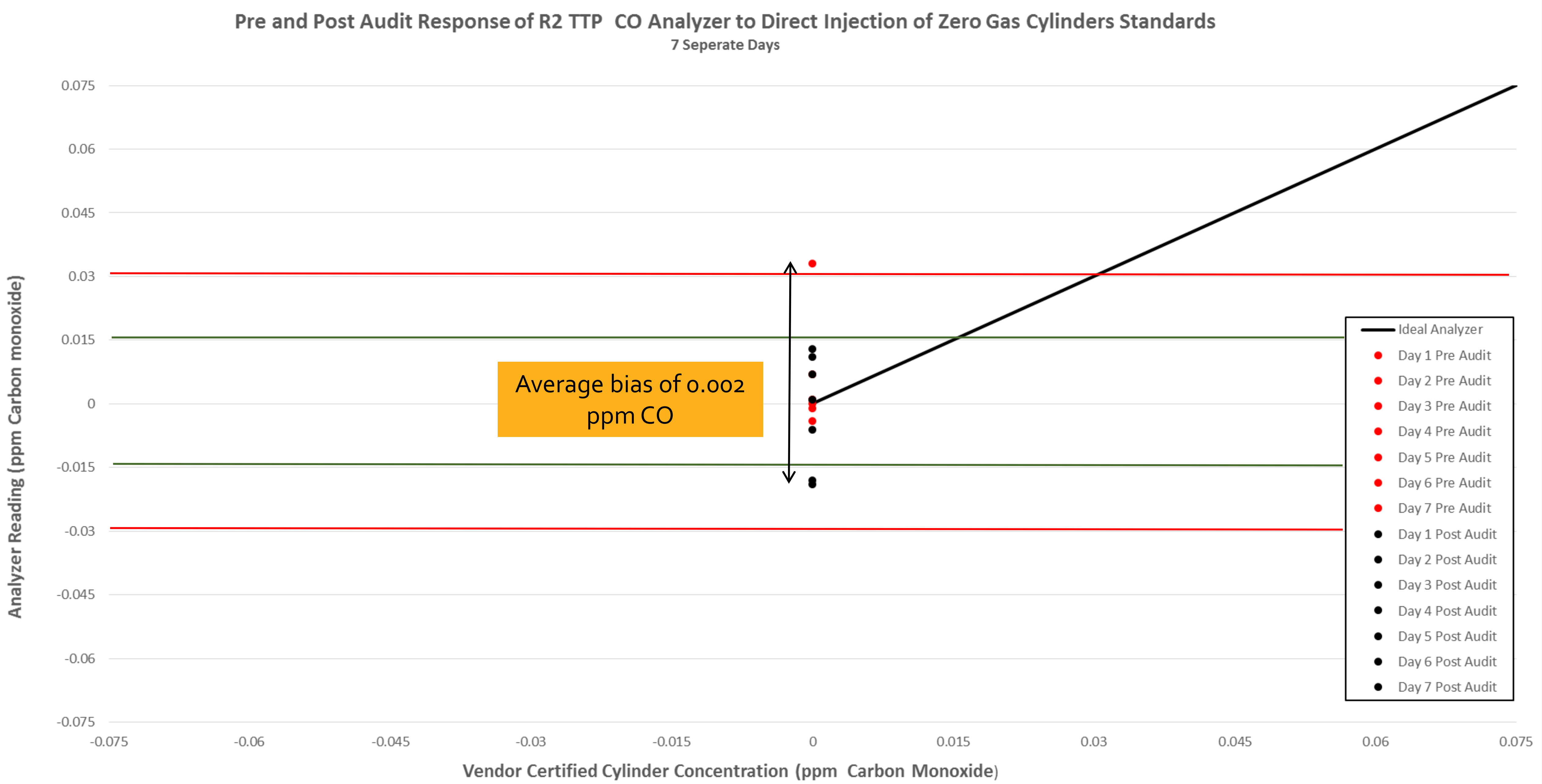
No Regression Correction for Drift – Precision Point Close Up



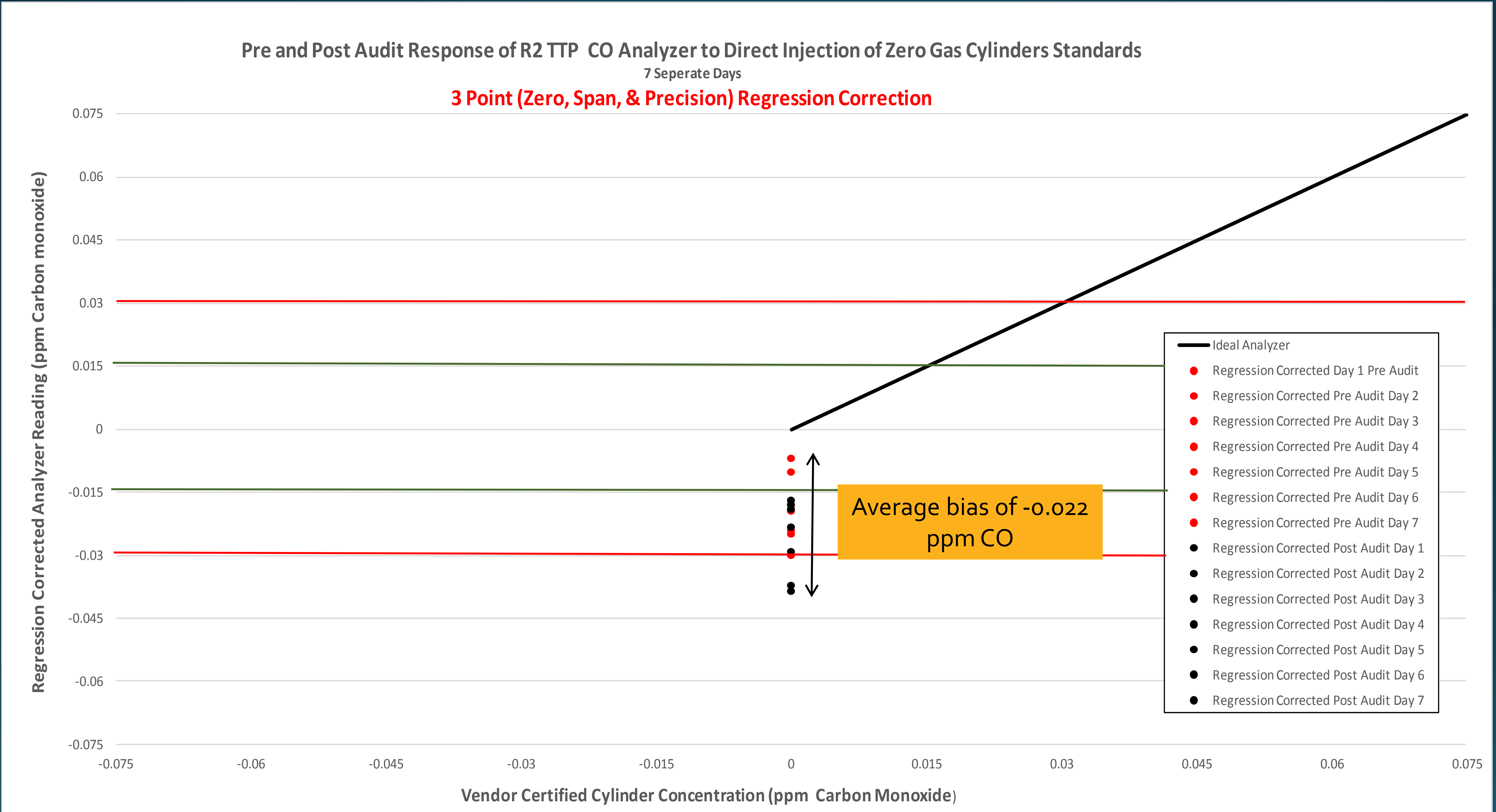
3 Point Regression Correction For Drift – Precision Point Close Up



No Regression Correction For Drift – Zero Point Close Up



3 Point Regression Correction For Drift – Zero Point Close Up



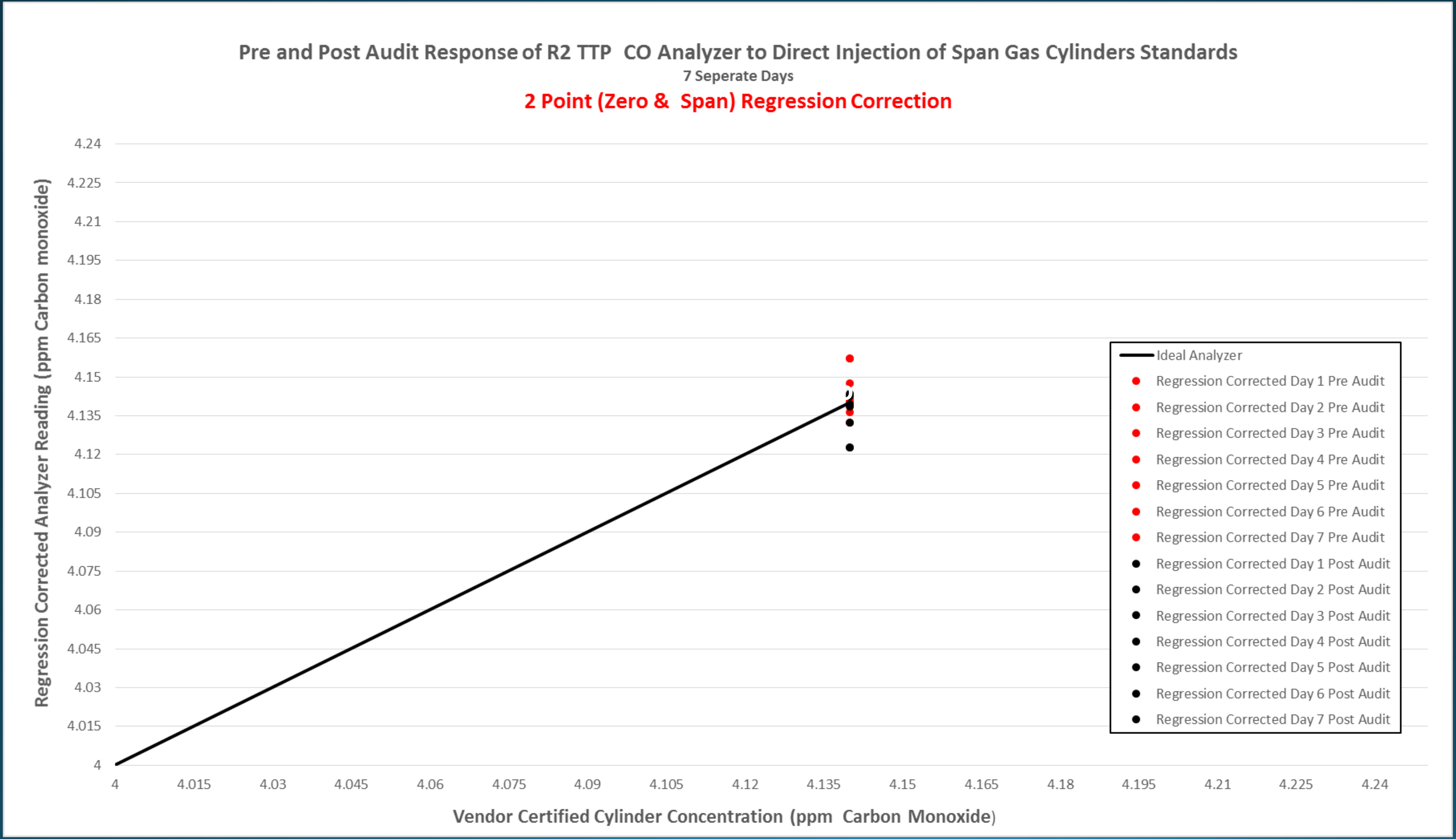
Finding #3

- Average precision point bias = +0.047 ppm CO (6.3%).
- Regression corrected average precision bias = +0.028 ppm CO (3.8%).
- Regression introduces a bias of – 0.022 ppm CO at all audit points. At audit concentrations <0.200 ppm, the acceptance criteria are ±0.030 ppm.

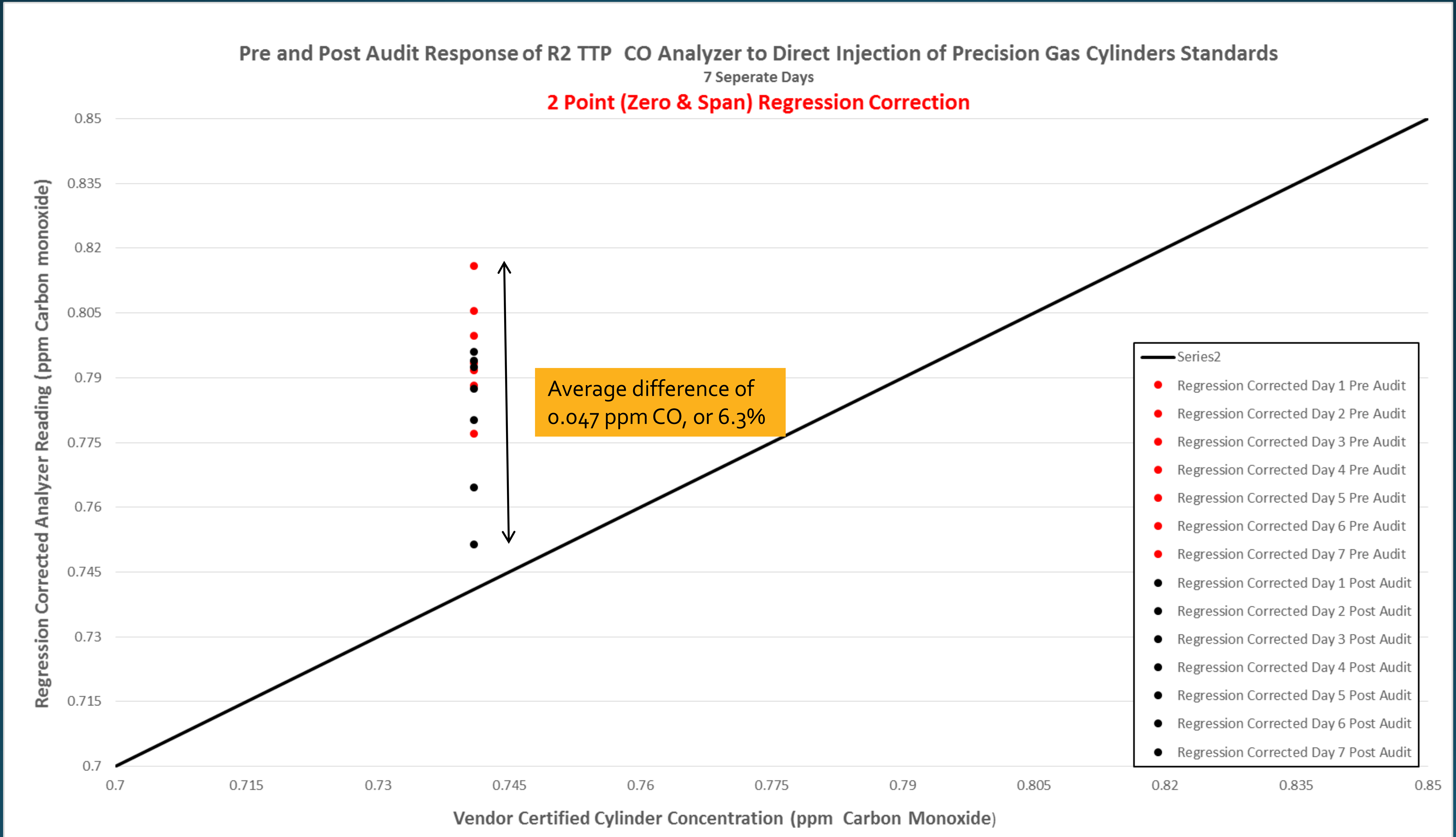
Question

How is a 2 point (span & zero) regression with this data?

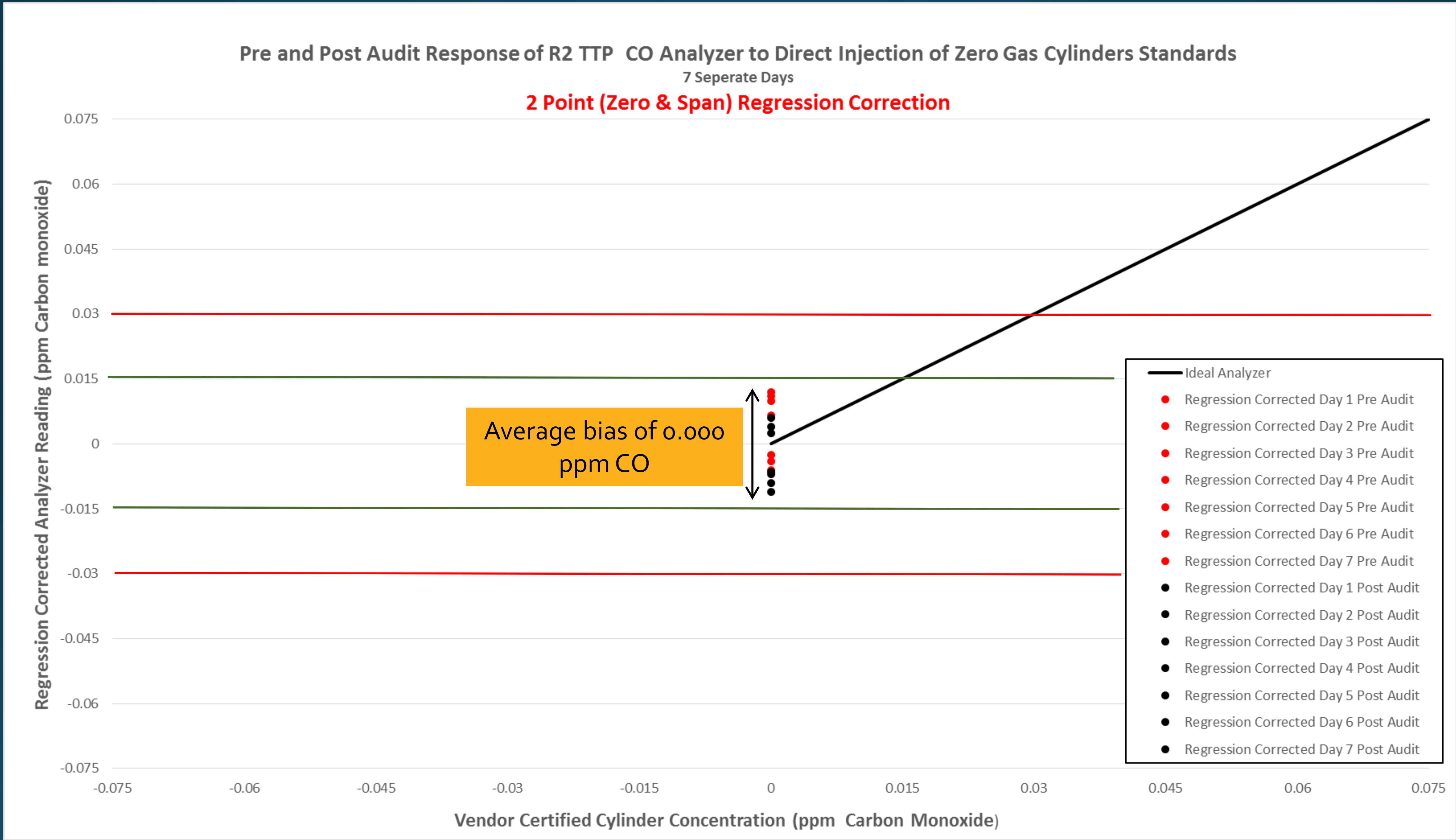
2 Point Regression Correction for Drift – Span Point Close Up



2 Point Regression Correction For Drift – Precision Point Close Up



2 Point Regression Correction For Drift – Zero Point Close Up



Finding #4

2 Point regression tightens the range at zero, but does not correct for the precision cylinder bias.

Comparison w/ Other Trace CO Analyzers

Is precision bias seen in other CO analyzers and precision gas standards?

With Region 1 assistance, 5 trace CO analyzers were assembled at Edison, NJ.

Analyzers were zeroed and calibrated by a flow certified GPT calibrator with a NIST SRM.

26 CO concentrations between 0-5 ppm were generated by GPT w/ the TTP multi-blend cylinder.

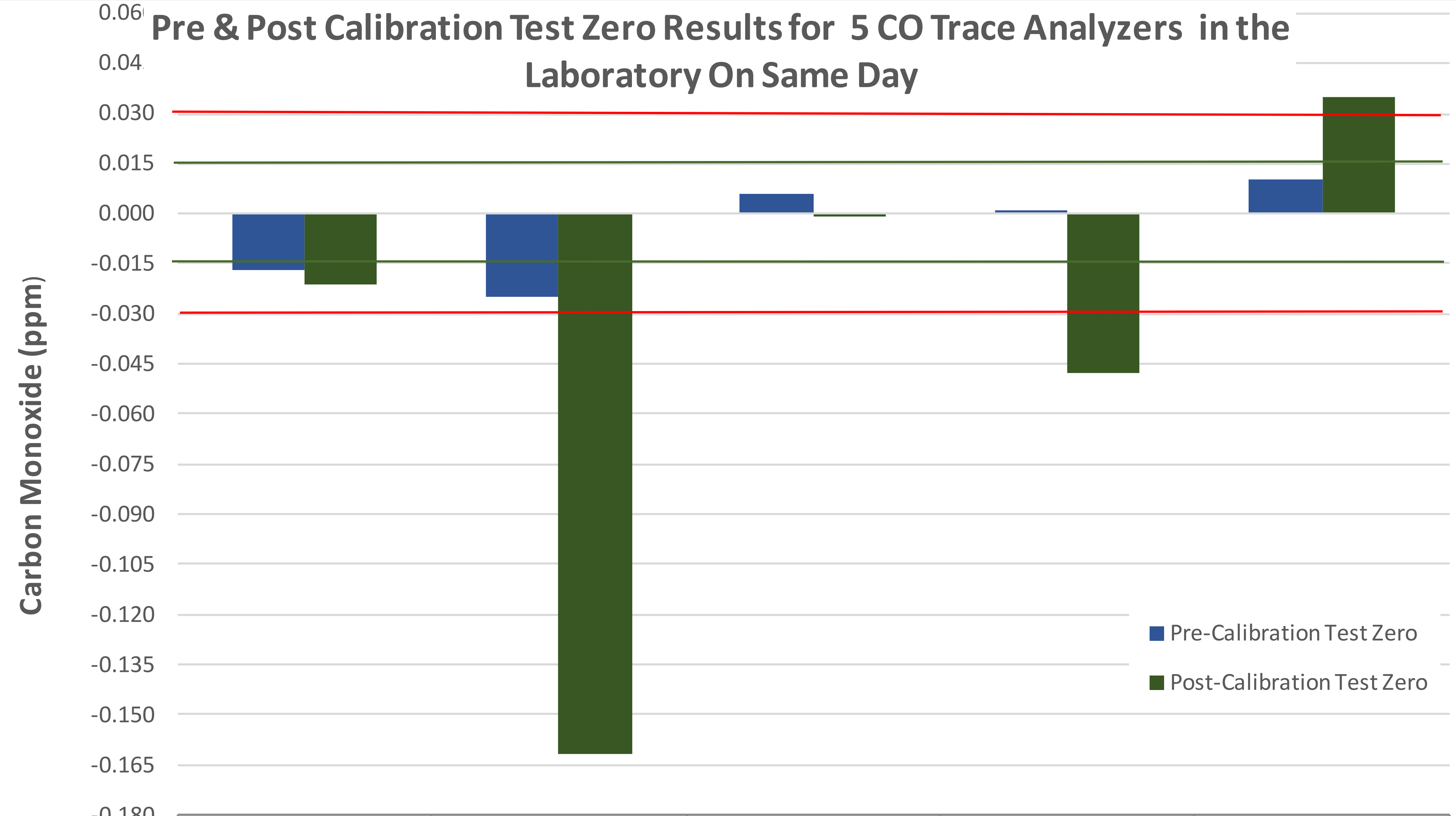
Region 1's undiluted span and precision standards were introduced to all analyzers, bracketed by similar concentrations generated by GPT.

Region 1 & 2 Prepare to Burn the Midnight Oil in Edison, NJ

Comparison w/ Other Trace CO Analyzers

Audit Points		GPT Settings			R2 TTP CO			R2 Rack CO #1			R2 Rack CO #2			R1 TTP CO #1			R1 TTP CO #2		
Audit Point #	Audit Point I	High MFC Setting (L/min)	Low MFC Setting (cc/min)	Expected Conc. (ppm)	CO ppm	% bias	Δ in ppm	CO ppm	% bias	Δ in ppm	CO ppm	% bias	Δ in ppm	CO ppm	% bias	Δ in ppm	CO ppm	% bias	Δ in ppm
1	Pre-Zero	20.0	0.0	0.000	-0.017		-0.017	-0.025		-0.025	0.006		0.006	0.001		0.001	0.010		0.010
2	NIST SRM F	20.0	20.0	4.889	4.879	-0.2%	-0.010	4.873	-0.3%	-0.016	4.884	-0.1%	-0.005	4.888	0.0%	-0.001	4.894	0.1%	0.005
3	LL108028	10.0	100.0	4.488	4.474	-0.3%	-0.014	4.468	-0.4%	-0.020	4.506	0.4%	0.018	4.529	0.9%	0.041	4.546	1.3%	0.058
4	LL108028	11.0	100.0	4.083	4.045	-0.9%	-0.038	4.089	0.2%	0.006	4.061	-0.5%	-0.022	4.110	0.7%	0.027	4.136	1.3%	0.053
5	LL111569	DIRECT INJECTION		4.050	4.024	-0.6%	-0.026	4.060	0.2%	0.010	4.046	-0.1%	-0.004	4.093	1.1%	0.043	4.105	1.4%	0.055
6	LL108028	13.0	100.0	3.458	3.422	-1.0%	-0.036	3.431	-0.8%	-0.027	3.454	-0.1%	-0.004	3.474	0.5%	0.016	3.511	1.5%	0.053
7	LL108028	15.0	100.0	2.999	2.959	-1.3%	-0.040	2.948	-1.7%	-0.051	2.982	-0.6%	-0.017	3.011	0.4%	0.012	3.059	2.0%	0.060
8	LL108028	18.0	100.0	2.502	2.446	-2.2%	-0.055	2.456	-1.8%	-0.046	2.478	-0.9%	-0.023	2.553	2.1%	0.051	2.506	0.2%	0.004
9	LL108028	20.0	90.0	2.028	1.982	-2.3%	-0.046	1.979	-2.4%	-0.049	2.010	-0.9%	-0.018	2.075	2.3%	0.047	2.027	0.0%	-0.001
10	LL108028	20.0	70.0	1.578	1.549	-1.8%	-0.029	1.497	-5.1%	-0.081	1.575	-0.2%	-0.003	1.624	2.9%	0.046	1.571	-0.4%	-0.007
11	LL108028	20.0	50.0	1.127	1.101	-2.3%	-0.026	1.058	-6.1%	-0.069	1.128	0.1%	0.001	1.112	-1.3%	-0.015	1.173	4.1%	0.046
12	LL108028	20.0	40.0	0.901	0.867	-3.8%	-0.034	0.820	-9.0%	-0.081	0.901	0.0%	0.000	0.934	3.7%	0.033	0.882	-2.1%	-0.019
13	LL108028	20.0	35.0	0.788	0.763	-3.2%	-0.025	0.678	-14.0%	-0.110	0.782	-0.8%	-0.006	0.763	-3.2%	-0.025	0.821	4.2%	0.033
14	LL111575	DIRECT INJECTION		0.750	0.760	1.3%	0.010	0.667	-11.1%	-0.083	0.771	2.8%	0.021	0.801	6.8%	0.051	0.753	0.4%	0.003
15	LL108028	20.0	30.0	0.675	0.656	-2.8%	-0.019	0.550	-18.5%	-0.125	0.666	-1.3%	-0.009	0.644	-4.6%	-0.031	0.708	4.9%	0.033
16	LL108028	20.0	25.0	0.562	0.538	-4.3%	-0.024	0.443	-21.2%	-0.119	0.557	-0.9%	-0.005	0.595	5.9%	0.033	0.526	-6.4%	-0.036
17	LL108028	20.0	20.0	0.449	0.423	-5.7%	-0.026	0.321	-28.5%	-0.128	0.441	-1.7%	-0.008	0.482	7.4%	0.033	0.414	-7.8%	-0.035
18	LL108028	20.0	15.0	0.336	0.318	-5.2%	-0.018	0.214	-36.2%	-0.122	0.326	-2.9%	-0.010	0.295	-12.1%	-0.041	0.368	9.7%	0.032
19	LL108028	20.0	10.0	0.222	0.199	-10.4%	-0.023	0.101	-54.5%	-0.121	0.213	-4.1%	-0.009	0.179	-19.4%	-0.043	0.242	8.9%	0.020
20	LL108028	20.0	8.0	0.177	0.151	-14.8%	-0.026	0.004	-97.8%	-0.173	0.167	-5.8%	-0.010	0.134	-24.4%	-0.043	0.202	14.0%	0.025
21	LL108028	20.0	6.0	0.132	0.108	-18.3%	-0.024	0.001	-99.2%	-0.131	0.122	-7.7%	-0.010	0.091	-31.2%	-0.041	0.159	20.3%	0.027
22	LL108028	20.0	5.0	0.110	0.083	-24.3%	-0.027	-0.033	-130.1%	-0.143	0.104	-5.1%	-0.006	0.063	-42.5%	-0.047	0.139	26.8%	0.029
23	LL108028	20.0	4.0	0.087	0.063	-27.7%	-0.024	-0.056	-164.3%	-0.143	0.075	-13.9%	-0.012	0.041	-52.9%	-0.046	0.116	33.2%	0.029
24	LL108028	20.0	3.0	0.065	0.043	-33.4%	-0.022	-0.094	-245.5%	-0.159	0.054	-16.4%	-0.011	0.019	-70.6%	-0.046	0.091	40.9%	0.026
25	LL108028	20.0	2.0	0.042	0.020	-52.5%	-0.022	-0.110	-361.3%	-0.152	0.035	-16.9%	-0.007	-0.003	-107.1%	-0.045	0.070	66.3%	0.028
26	LL108028	20.0	1.5	0.031	0.014	-54.5%	-0.017	-0.113	-466.9%	-0.144	0.025	-18.8%	-0.006	-0.017	-155.2%	-0.048	0.062	101.3%	0.031
27	NIST SRM F	20.0	20.0	4.889	4.859	-0.6%	-0.030	4.731	-3.2%	-0.158	4.871	-0.4%	-0.018	4.832	-1.2%	-0.057	4.922	0.7%	0.033
28	Zero	20.0	0.0	0.000	-0.021		-0.021	-0.162		-0.162	-0.001		-0.001	-0.048		-0.048	0.035		0.035

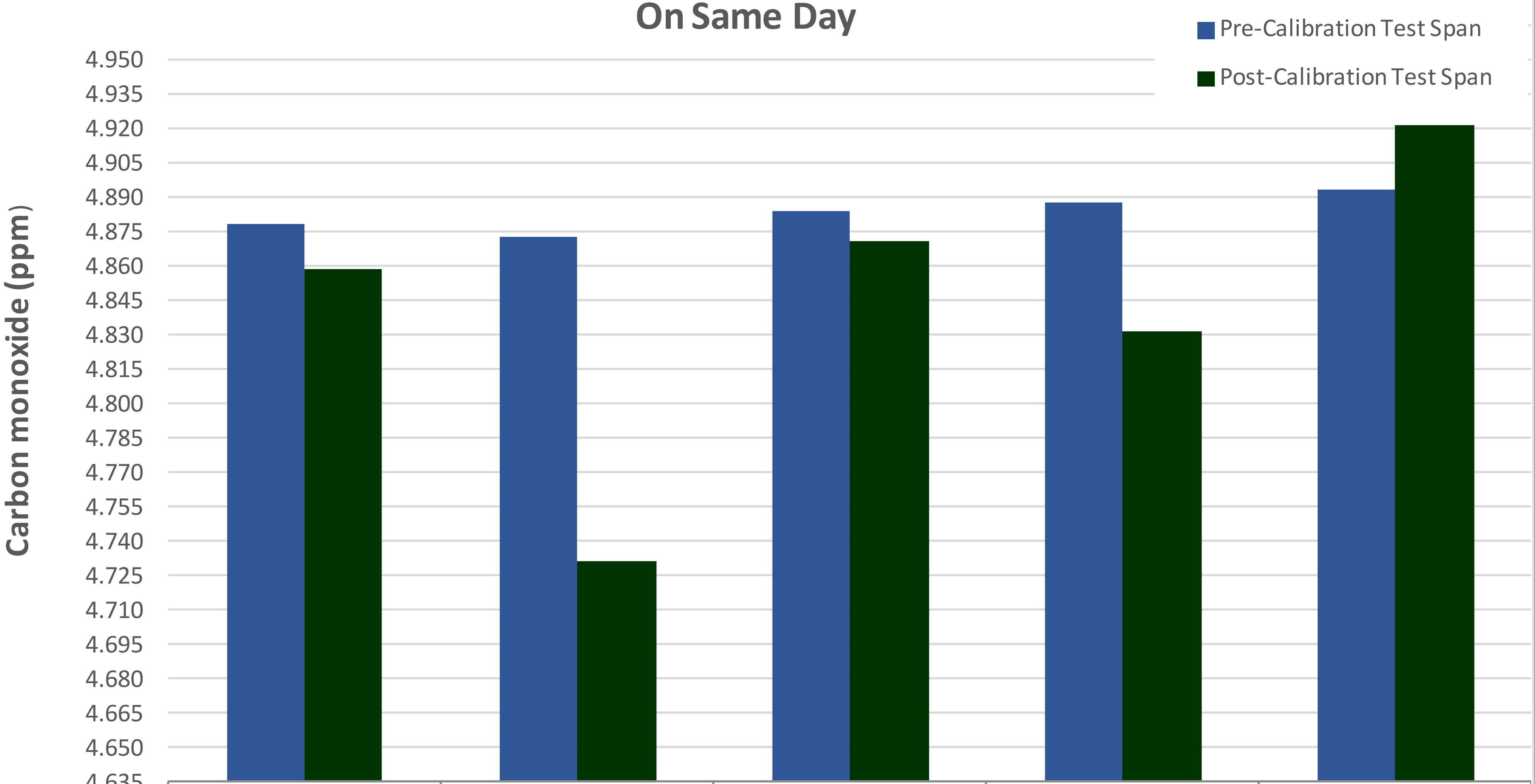
Comparison w/ Other CO Analyzers – Zero



	R2 TTP CO	R2 Rack CO #1	R2 Rack CO #2	R1 TTP CO #1	R1 TTP CO #2
Pre-Calibration Test Zero	-0.017	-0.025	0.006	0.001	0.010
Post-Calibration Test Zero	-0.021	-0.162	-0.001	-0.048	0.035

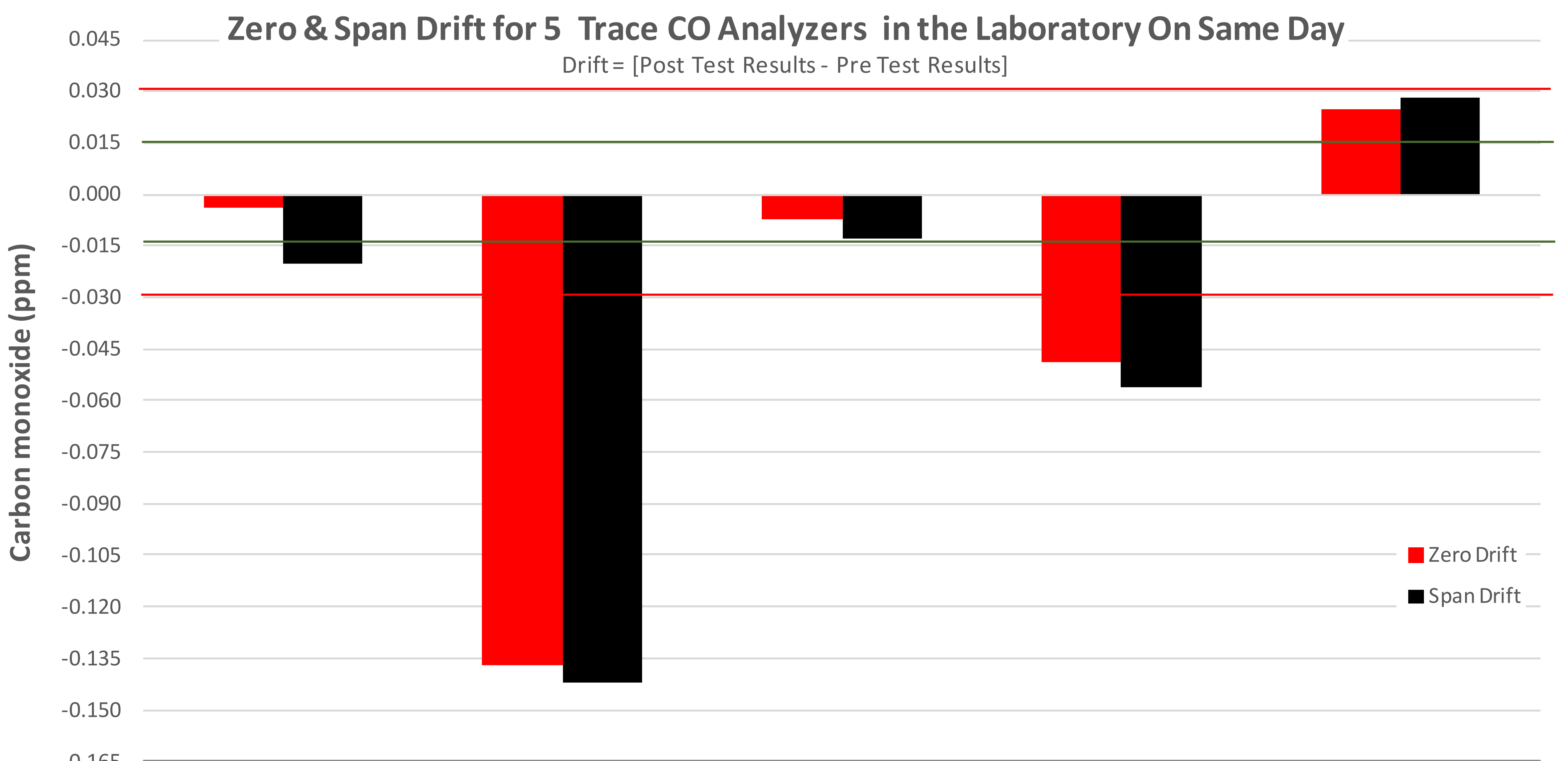
Comparison w/ Other CO Analyzers - Span

Pre & Post Calibration Test Span Results for 5 Trace CO Analyzers in the Laboratory On Same Day



	R2 TTP CO	R2 Rack CO #1	R2 Rack CO #2	R1 TTP CO #1	R1 TTP CO #2
Pre-Calibration Test Span	4.879	4.873	4.884	4.888	4.894
Post-Calibration Test Span	4.859	4.731	4.871	4.832	4.922

Comparison w/ Other CO Analyzers - Drift



	R2 TTP CO	R2 Rack CO #1	R2 Rack CO #2	R1 TTP CO #1	R1 TTP CO #2
Zero Drift	-0.004	-0.137	-0.007	-0.049	0.025
Span Drift	-0.020	-0.142	-0.013	-0.056	0.028

Comparison w/ Other CO Analyzers

Finding #5

Drift varies by analyzer, even with the same manufacturer and model.

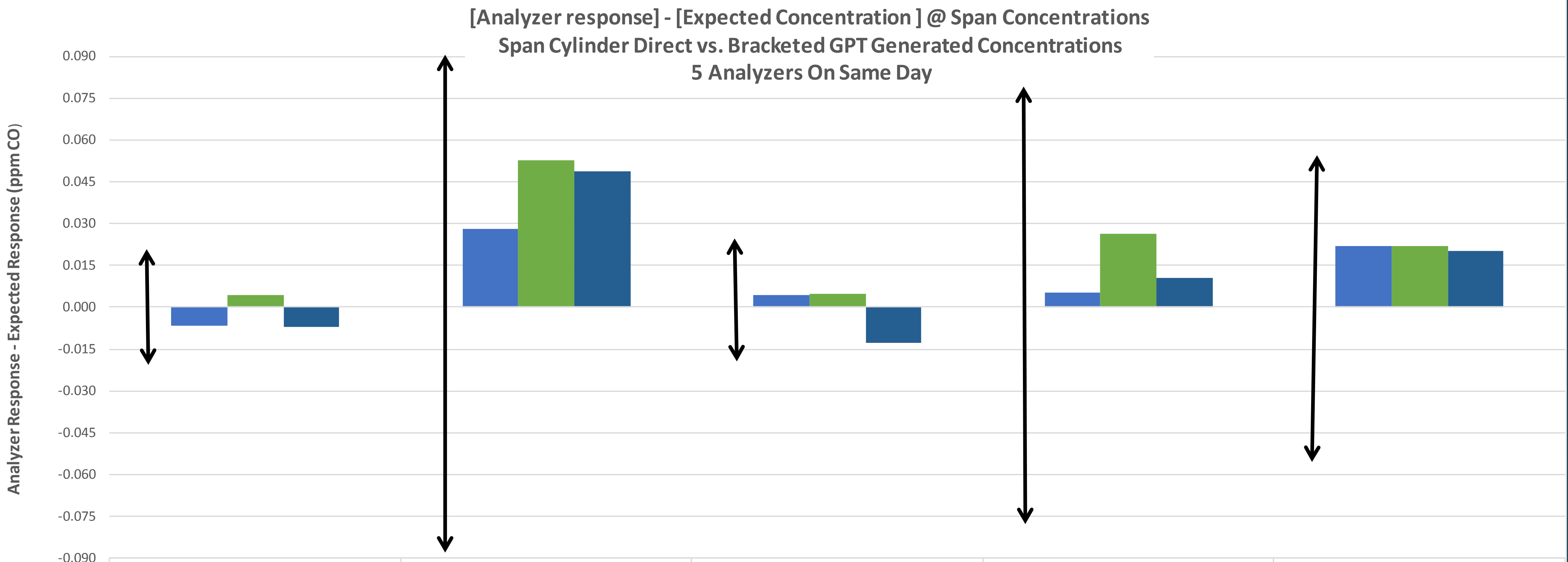
Again, zero & span drift were had the same relative magnitude and direction.

2 out of the 5 analyzers did not meet audit acceptance criteria of ±0.030 ppm at concentrations below 0.200 ppm CO.

Comparison w/ Other CO Analyzers

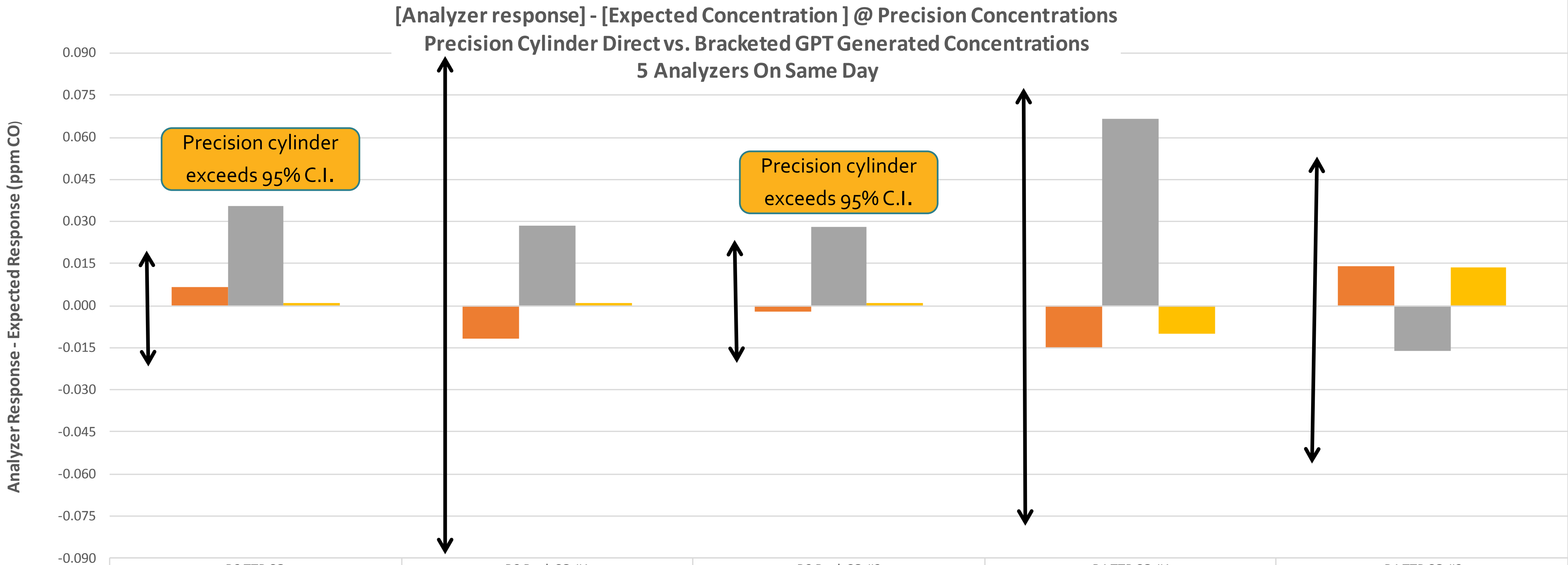
How did the span and precision standards fare against the bracketed GPT generated concentrations?

Comparison w/ Other CO Analyzers – Span Cylinder Direct vs. GPT



	R2 TTP CO Difference relative to expected (ppm CO)	R2 Rack CO #1 Difference relative to expected (ppm CO)	R2 Rack CO #2 Difference relative to expected (ppm CO)	R1 TTP CO #1 Difference relative to expected (ppm CO)	R1 TTP CO #2 Difference relative to expected (ppm CO)
3.458 ppm CO GPT	-0.007	0.028	0.004	0.005	0.022
4.050 ppm CO w/ Span Cylinder	0.004	0.053	0.005	0.026	0.022
4.083 ppm CO GPT	-0.007	0.049	-0.013	0.010	0.020
95% Confidence Interval	0.021 ppm CO	0.090 ppm CO	0.019 ppm CO	0.076 ppm CO	0.055 ppm CO
Slope	0.99855	1.0206	0.99947	1.0097	1.00422
Intercept	-0.0245	-0.12731	-0.00669	-0.02267	0.01616

Comparison w/ Other CO Analyzers – Precision Cylinder Direct vs. GPT



	R2 TTP CO Difference relative to expected (ppm CO)	R2 Rack CO #1 Difference relative to expected (ppm CO)	R2 Rack CO #2 Difference relative to expected (ppm CO)	R1 TTP CO #1 Difference relative to expected (ppm CO)	R1 TTP CO #2 Difference relative to expected (ppm CO)
0.675 ppm CO GPT	0.007	-0.012	-0.002	-0.015	0.014
0.750 ppm CO w/ Precision Cylinder	0.036	0.029	0.028	0.066	-0.016
0.788 ppm CO GPT	0.001	0.001	0.001	-0.010	0.014

95% Confidence Interval	0.021 ppm CO	0.090 ppm CO	0.019 ppm CO	0.076 ppm CO	0.055 ppm CO
Slope	0.99855	1.0206	0.99947	1.0097	1.00422
Intercept	-0.0245	-0.12731	-0.00669	-0.02267	0.01616

Finding #6

All 5 analyzers showed span cylinder response within the 95% C.I.

2 out of 5 analyzers showed precision cylinder response outside the 95% C.I.

4 out of 5 analyzers showed precision cylinder response departed from expectations > 2x GPT derived points @ similar concentrations.

Only 2 of the 5 analyzers had a 95% confidence interval < 0.030 ppm CO.

Implications

Precision CO standard cylinder concentration may be in error.

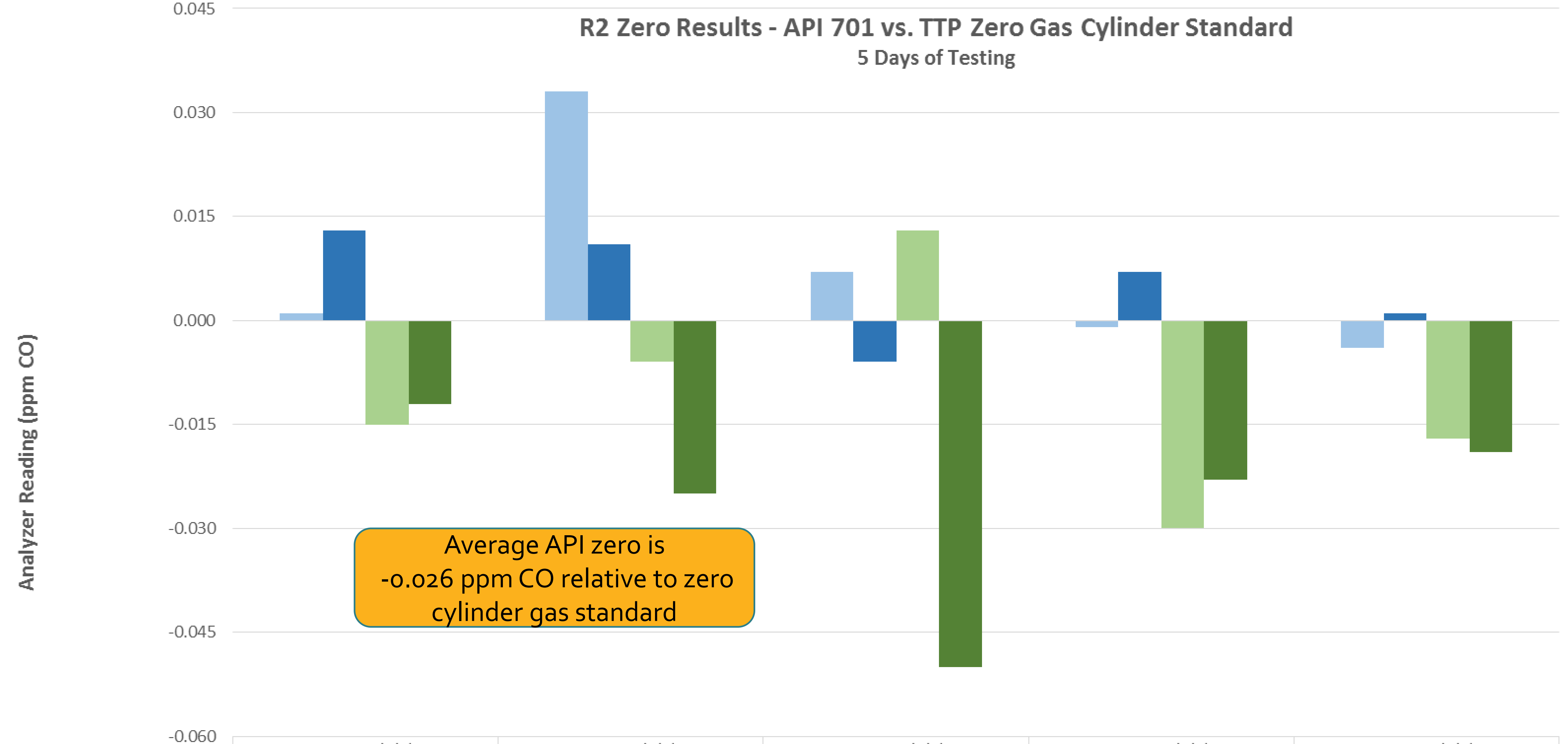
Span standard & multi-blend audit cylinder concentrations appear accurate.

Zero Cylinder Gas Purity

Zero Gas Cylinder Purity was tested as follows:

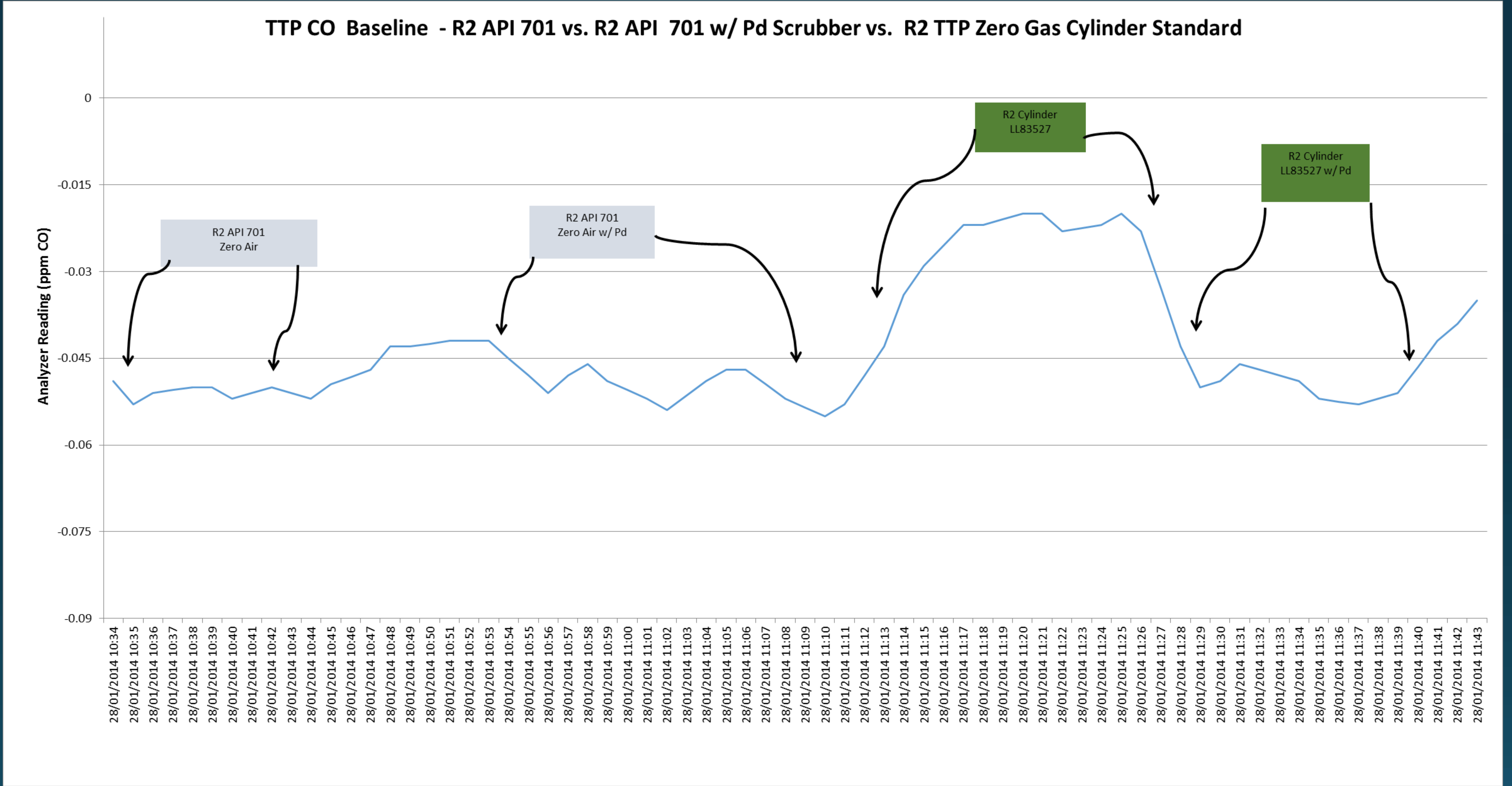
- CO Analyzer calibrated with gas cylinder zero.
- API zero air generator is used to generate zero gas.
- API zero & cylinder zero gas results are compared.
- Zero gas standards cylinders and API 701 zero air supply were assayed with and without a palladium scrubbers.

Zero

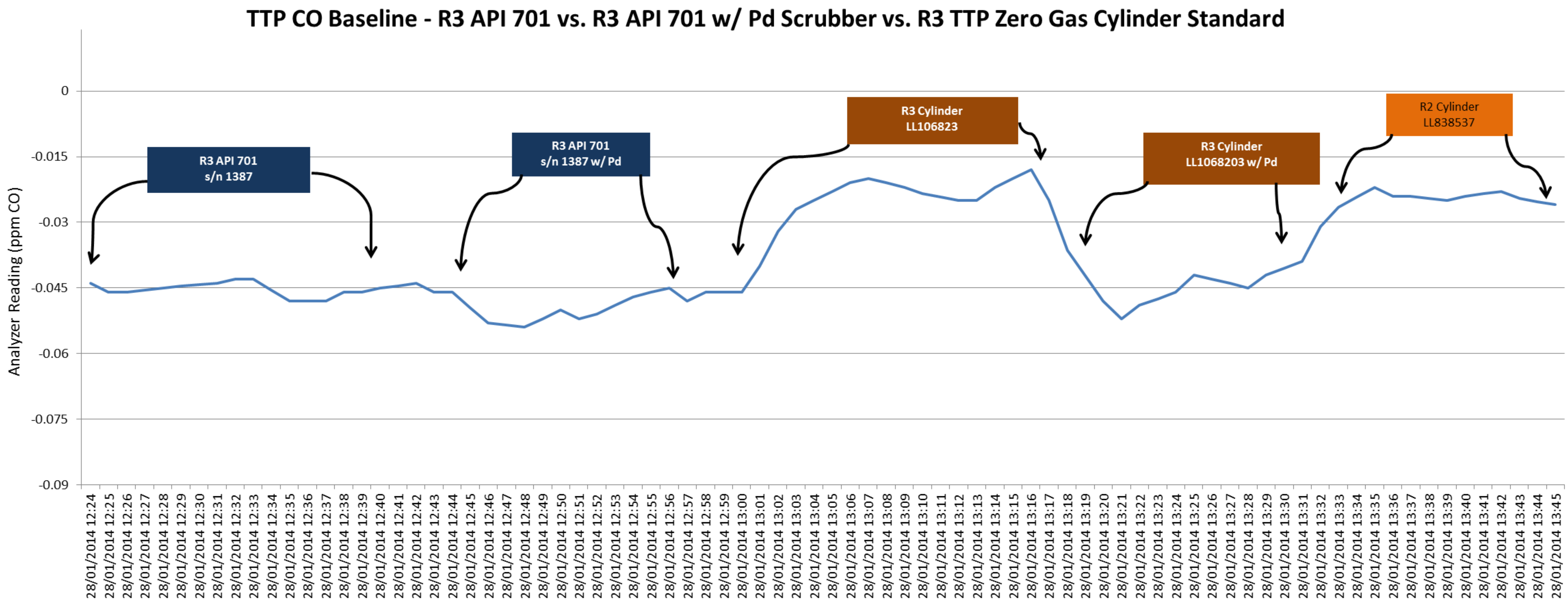


	Day 1 - Air lab	Day 2- Air lab	Day 3 - Air lab	Day 4 - Air lab	Day 5 - Air lab
Zero Gas Cylinder Pre Audit	0.001	0.033	0.007	-0.001	-0.004
Zero Gas Cylinder Post Audit	0.013	0.011	-0.006	0.007	0.001
API 701 Zero Gas Pre Audit	-0.015	-0.006	0.013	-0.030	-0.017
API 701 Zero Gas Post Audit	-0.012	-0.025	-0.050	-0.023	-0.019

Purity of Zero Gas Cylinder Standard



Zero



TTP CO Baseline - R3 API 701 vs. R3 API 701 w/ Pd Scrubber vs. R3 TTP Zero Gas Cylinder Standard
Analyzer Reading (ppm CO)
0
-0.015
-0.03
-0.045
-0.06
-0.075
-0.09
R3 API 701 s/n 1387
R3 API 701 s/n 1387 w/ Pd
R3 Cylinder LL106823
R3 Cylinder LL1068203 w/ Pd
R2 Cylinder LL838537
28/01/2014 12:24
28/01/2014 13:45

Finding #7

API zero gas generator averages -0.026 ppm < CO than zero gas cylinder standard.

Zero gas standard cylinder with Pd scrubber removes 0.020 to 0.030 ppm CO.

Zero gas cylinder + Pd scrubber was = API zero gas generator results.

This holds true for EPA R3 system, R2 system, and R1 system.

Implication

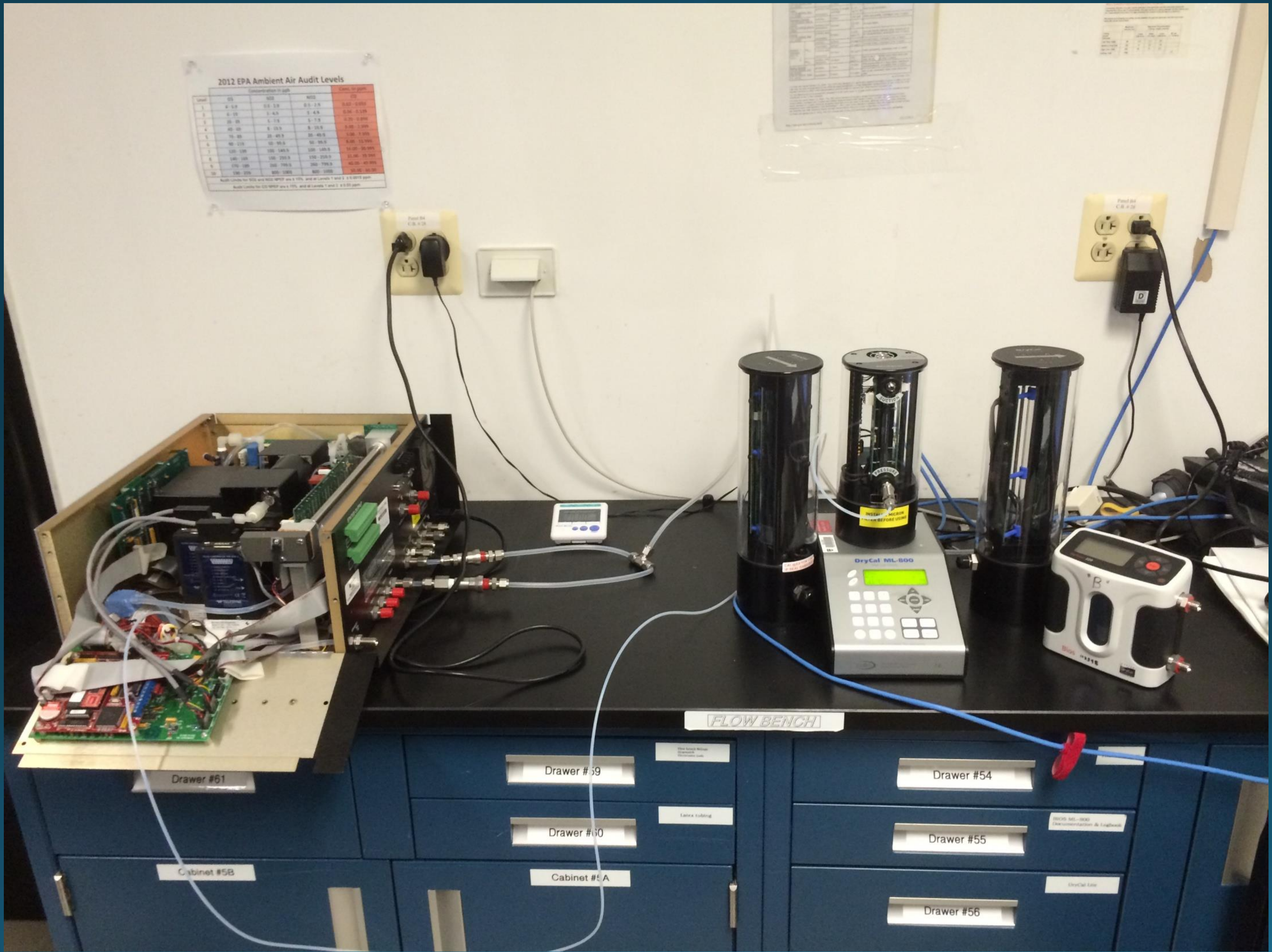
Zero gas is contaminated w/ 0.020 – 0.030 ppm CO.

Pd scrubbers can be used with the stock API zero gas systems, and the use of zero gas cylinders eliminated.

CO Analyzer vs. Flow Controller Derived Audit Gas Concentrations In the Laboratory

1. Use improved correction techniques for CO analyzer performance, including:
   - 2 point regression curve (zero & span)
   - API zero air used as the "true" basis for zero

2. Compare certified flow controller derived CO audit concentrations w/ corrected CO analyzer derived concentrations.



2012 EPA Ambient Air Audit Levels
DryCal ML-800
FLOW BENCH
Drawer #61
Drawer #54
Drawer #55
Drawer #56
Cabinet #5B

Corrected Carbon Monoxide Analyzer vs. Mass Flow Controller

Flow Calibration Data

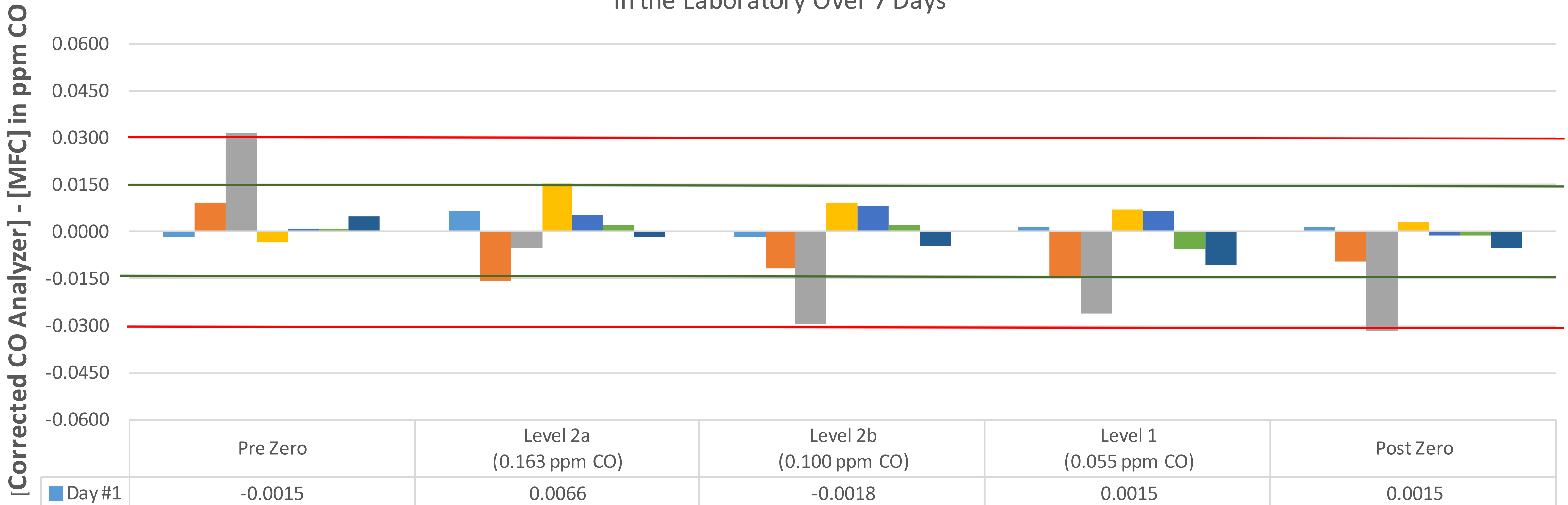
February 1, 2013

Zero Gas Mass Flow Controller (20,000 cc/min Capacity)					Pollutant Gas Mass Flow Controller (100 cc/min capacity)					Pollutant Gas Mass Flow Controller (10.0 cc/min capacity)				
MFC Setting (L/min)	MFC Reading (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Curve Predicted	% error in curve prediction	MFC Setting (cc/min)	MFC Reading (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Curve Predicted	% error in curve prediction	MFC Setting (cc/min)	MFC Reading (cc/min)	Actual Flow (cc/min @ 760 mm	Curve Predicted	% error in curve prediction
20000	19983	20094	20093	0.00%	100	99.91	100.14	100.12	-0.02%	10	9.99	9.96	9.95	-0.08%
16000	15990	16068	16067	0.00%	80	79.34	80.02	80.08	0.07%	7.5	7.99	7.43	7.44	0.16%
12000	11991	12041	12041	0.00%	60	59.96	60.10	60.05	-0.08%	5	6.00	4.94	4.94	-0.02%
										2.5	3.99	2.43	2.43	-0.05%
8000	7991	8012	8016	0.05%	40	39.96	40.00	40.01	0.02%	1.25	1.99	1.18	1.18	-0.14%
4000	3991	3991	3990	-0.02%										
2500	2494	2482	2481	-0.07%	20	19.95	19.98	19.98	-0.01%					
					10.5	10.95	10.45	10.46	0.04%					
4000														
Zero MFC Slope		1.0064	Slope Accuracy	1.0000	Slope		1.0018	Slope Accuracy	1.0000	Slope		1.0021	Slope Accuracy	1.0000
Zero MFC Intercept		-35.5409	Intercept Accuracy	0.0008	Intercept		-0.0599	Intercept Accuracy	0.0001	Intercept		-0.0737	Intercept Accuracy	0.00002

Corrected CO Analyzer vs. Mass Flow Controller – In the Lab

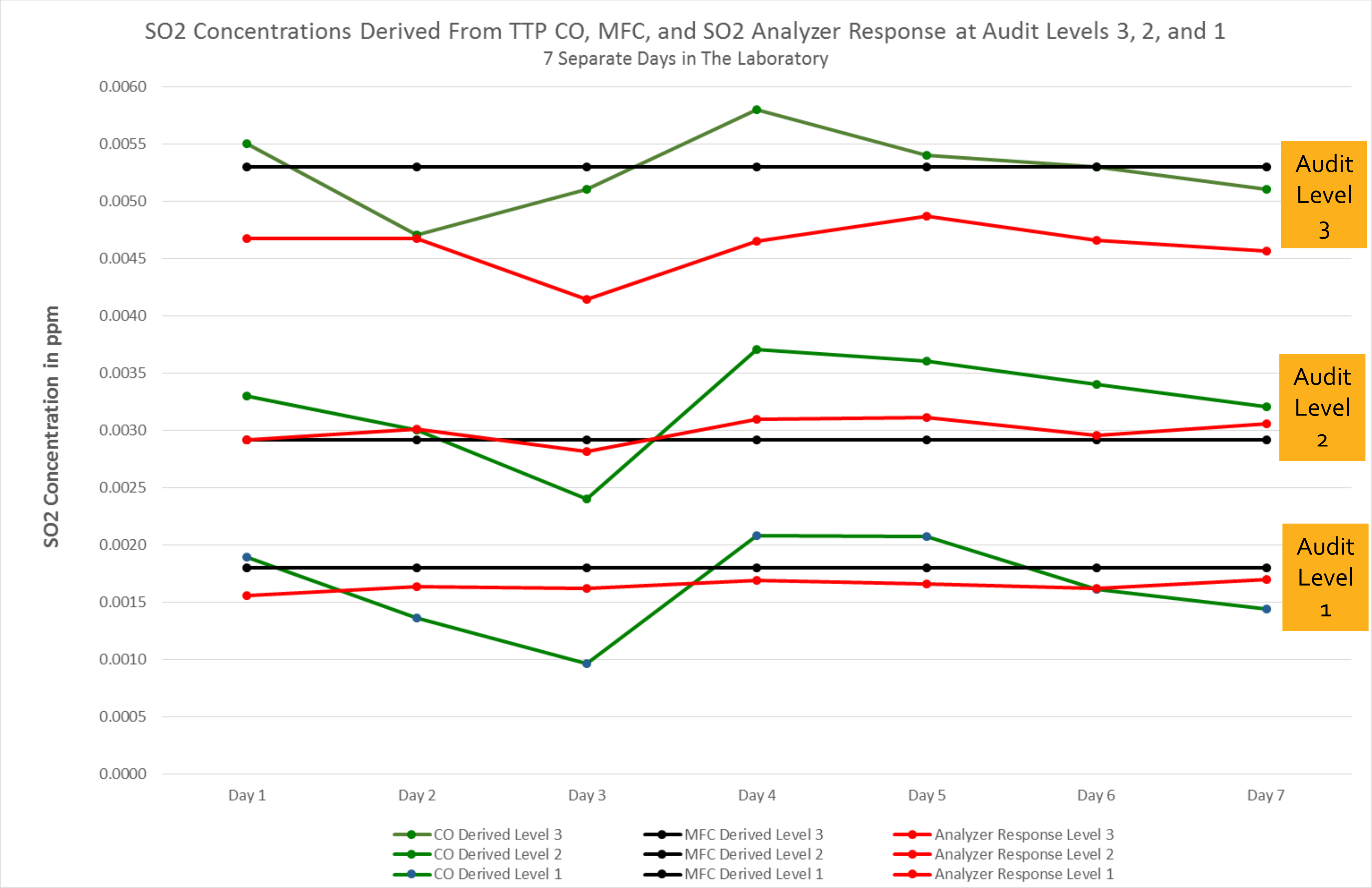
[Corrected CO Analyzer] - [Mass Flow Controller Derived CO Concentrations] at Pre & Post Zero and @ Audit Levels < 0.200 ppm CO

In the Laboratory Over 7 Days



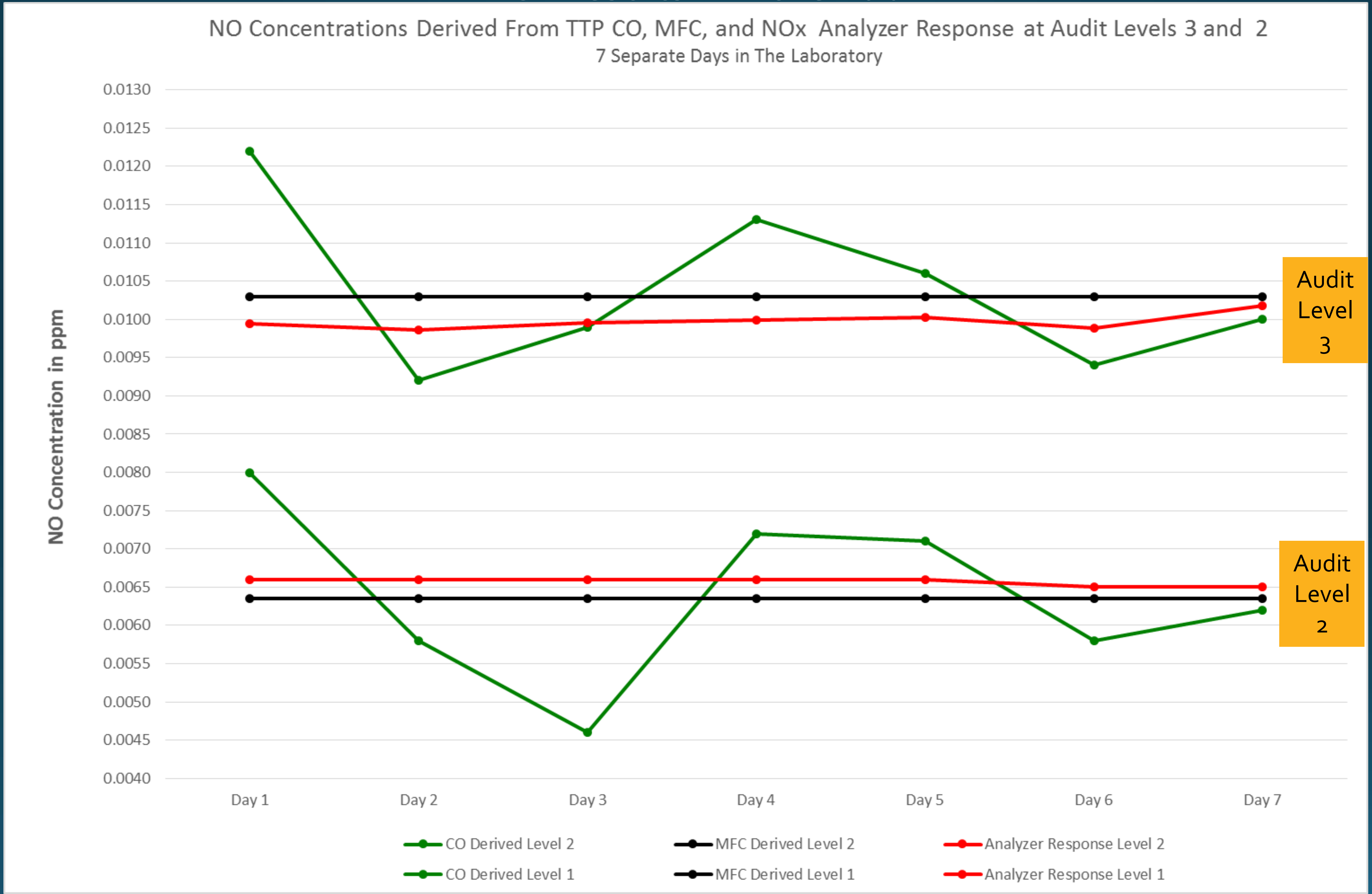
	Pre Zero	Level 2a (0.163 ppm CO)	Level 2b (0.100 ppm CO)	Level 1 (0.055 ppm CO)	Post Zero
Day #1	-0.0015	0.0066	-0.0018	0.0015	0.0015
Day #2	0.0095	-0.0153	-0.0118	-0.0144	-0.0095
Day #3	0.0315	-0.0048	-0.0295	-0.0263	-0.0315
Day #4	-0.0035	0.0157	0.0096	0.0072	0.0035
Day #5	0.0010	0.0056	0.0084	0.0068	-0.0010
Day #6	0.0010	0.0019	0.0023	-0.0055	-0.0010
Day #7	0.0050	-0.0018	-0.0045	-0.0104	-0.0050

Corrected CO Analyzer vs. Flow Controller SO_2 results – In the Lab



Corrected CO Analyzer vs. Flow Controller

NOx results – In the Lab



Finding #8

In the lab, NOx and SO_2 analyzer responses were closer to MFC derived concentrations than corrected CO analyzer derived concentrations. This was more strongly evident at lower audit concentrations.

In the laboratory, [Corrected CO] - [MFC derived CO concentrations]

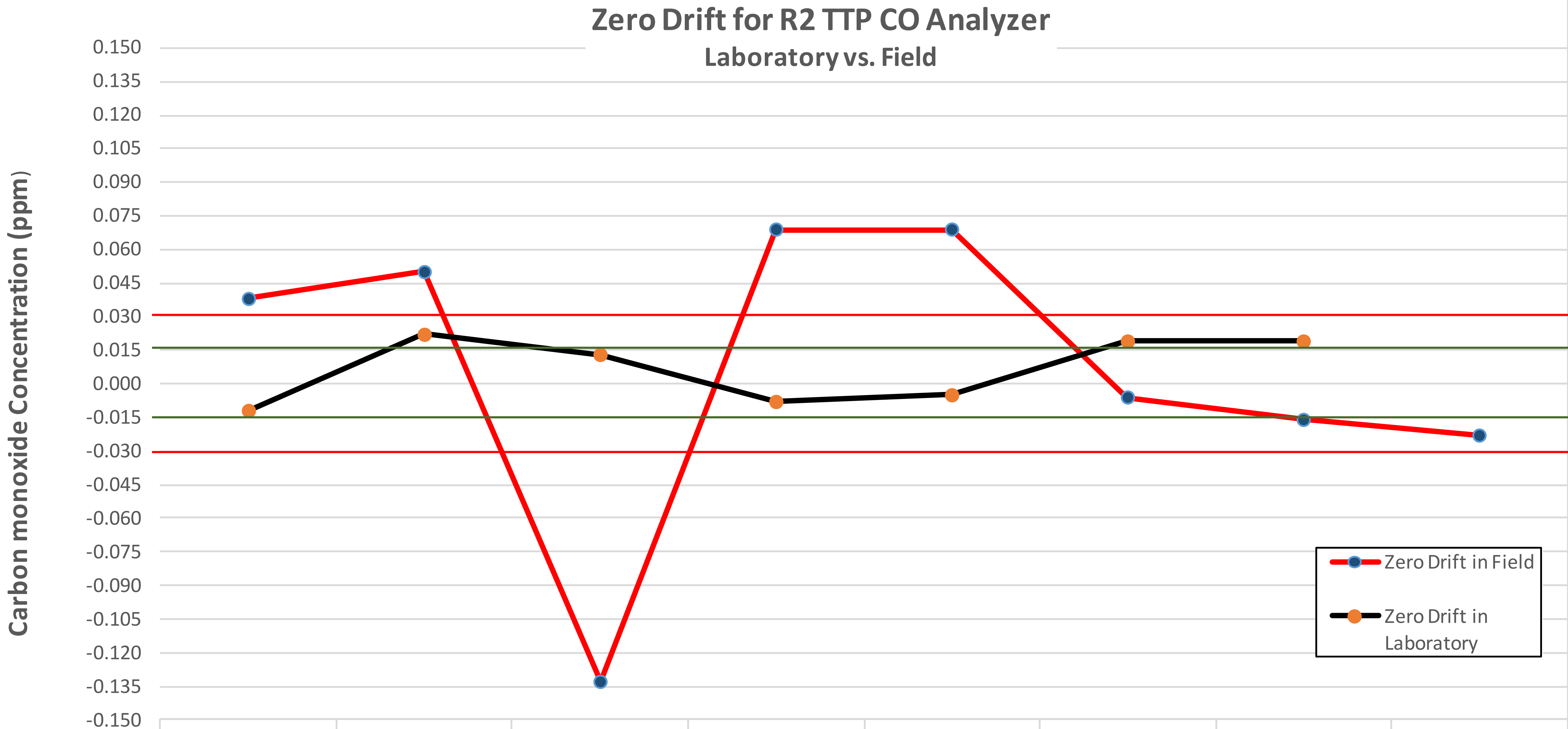
were typically within ± 0.015 ppm CO, although this was exceeded on occasion.

CO Analyzer vs. Flow Controller Derived Audit Gas Concentrations In the Field

Trace level audits were performed at 4 Ncore sites in Region 2.

Each Ncore site required 2 days of auditing, and the TTP system was recalibrated each day.

In the Field – Zero Drift



	Instance #1	Instance #2	Instance #3	Instance #4	Instance #5	Instance #6	Instance #7	Instance #8
Zero Drift in Field	0.038	0.05	-0.133	0.069	0.069	-0.006	-0.016	-0.023
Zero Drift in Laboratory	-0.012	0.022	0.013	-0.008	-0.005	0.019	0.019	

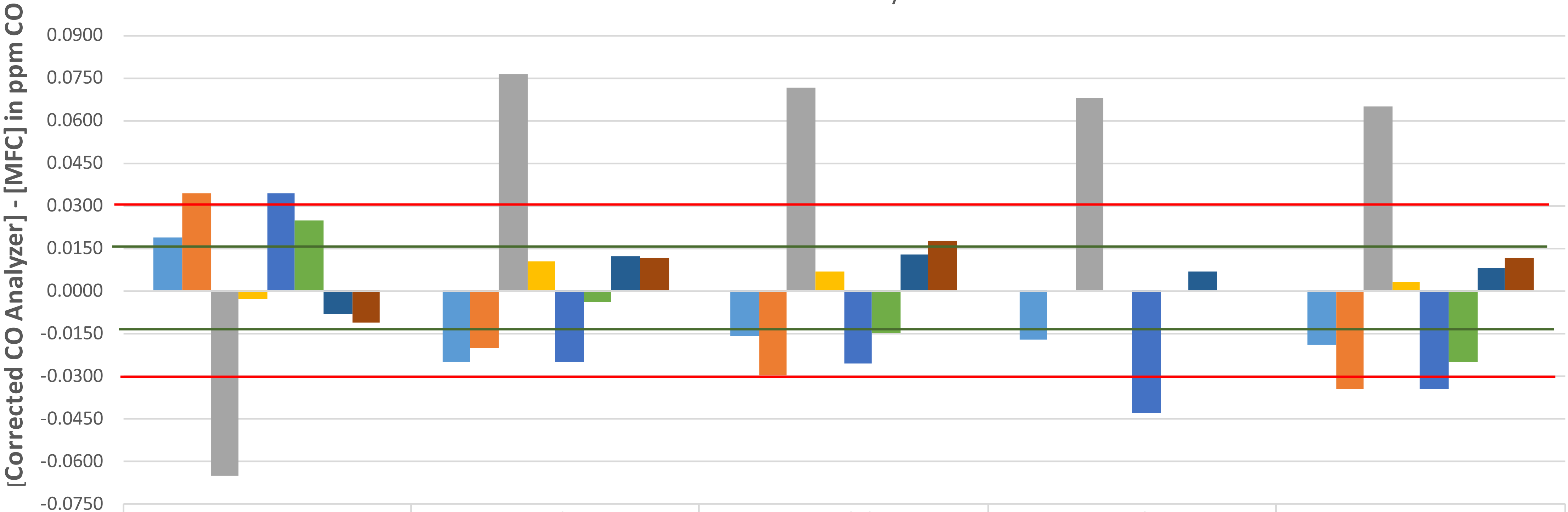
Finding #9

In the field, CO analyzer drift was > ±0.030 ppm CO on 5 out of 8 days, and >±0.015 ppm CO on 7 of 8 days.

In the laboratory, zero drift exceeded ±0.030 ppm CO once, and ±0.015 CO was exceeded on 3 of 7 days.

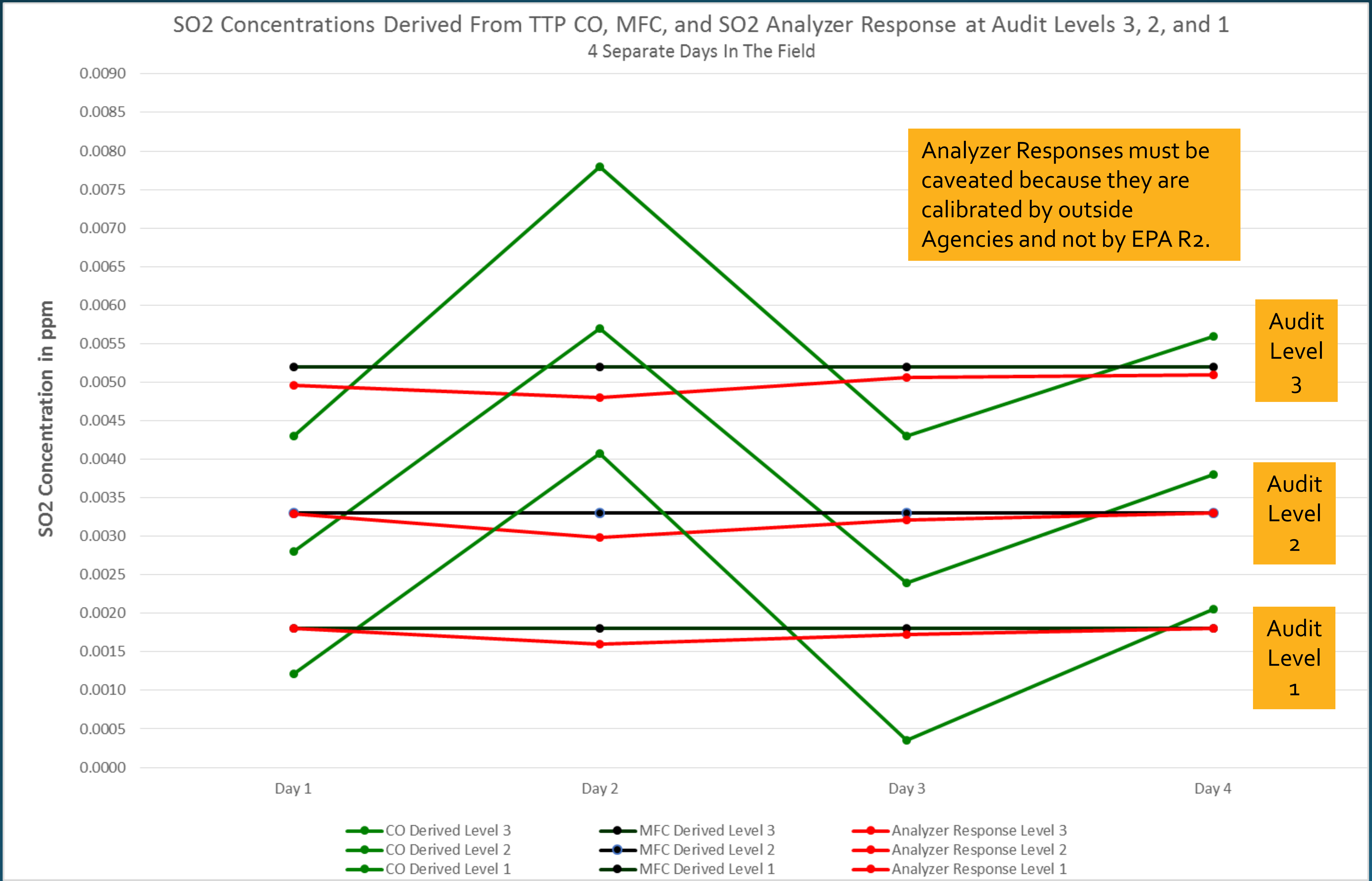
CO Analyzer vs. Mass Flow Controller – In The Field

[Corrected CO Analyzer] - [Mass Flow Controller Derived CO Concentrations]
at Pre & Post Zero and @ Audit Levels < 0.200 ppm CO
In the Field Over 8 Days

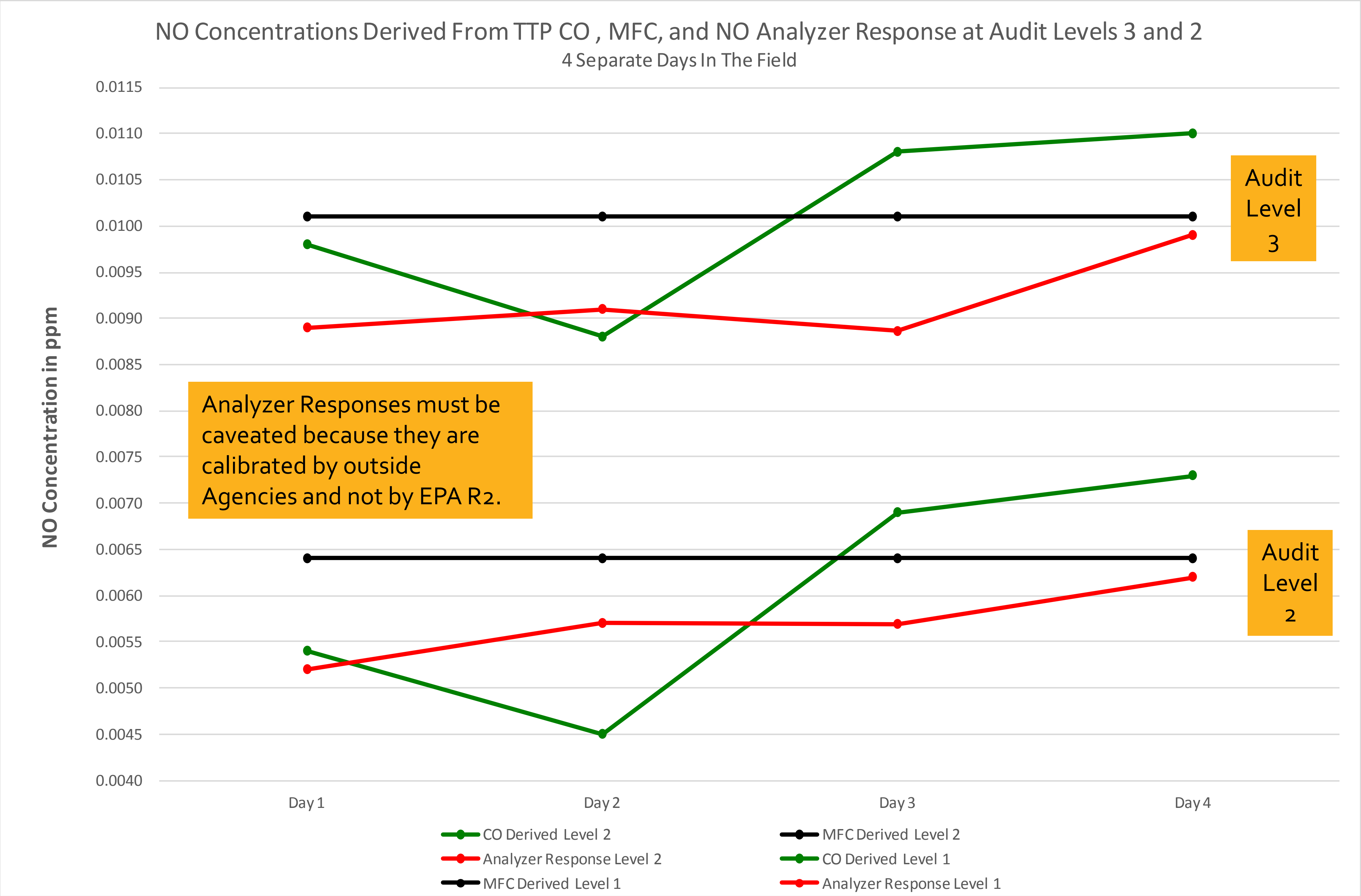


	Pre Zero	Level 2a (0.163 ppm CO)	Level 2b (0.100 ppm CO)	Level 1 (0.055 ppm CO)	Post Zero
Day 1	0.0190	-0.0251	-0.0160	-0.0171	-0.0190
Day 2	0.0345	-0.0202	-0.0299		-0.0345
Day 3	-0.0652	0.0762	0.0717	0.0677	0.0652
Day 4	-0.0030	0.0103	0.0066		0.0030
Day 5	0.0344	-0.0253	-0.0259	-0.0427	-0.0344
Day 6	0.0250	-0.0042	-0.0151		-0.0250
Day 7	-0.0080	0.0124	0.0127	0.0067	0.0080
Day 8	-0.0114	0.0116	0.0173		0.0114

CO Analyzer vs. Mass Flow Controller – In the Field



CO Analyzer vs. Mass Flow Controller – In the Field



Finding #10

The difference between:

[CO analyzer determined concentrations] – [Mass Flow Controller derived Concentrations]

was > in the field than in the laboratory.

Proposed Draft Future Steps w/ Current Equipment

Current	Proposed
Zero gas cylinder standard	Zero Air supply w/ palladium
Span gas cylinder run pre & post audit	Span gas cylinder only @ pre audit
Precision cylinder for calibration purposes	Not Used
CO analyzer zero @ pre audit only	CO analyzer zero @ every point < 1.0 ppm
Regression correction w/ pre & post zero/span/precision	No regression – re zero @ all low audit points

Reason - Zero gas cylinder contaminated with ~ 0.020 ppm CO

Proposed Draft Future Steps w/ Current Equipment

Current	Proposed
Zero gas cylinder standard	Zero Air supply w/ palladium
Span gas cylinder run pre & post audit	Span gas cylinder only @ pre audit
Precision cylinder for calibration purposes	Not Used
CO analyzer zero @ pre audit only	CO analyzer zero @ every point < 1.0 ppm
Regression correction w/ pre & post zero/span/precision	No regression – re zero @ all low audit points

Reason – Span drift at the end of the audit can be compensated with zero drift correction

Proposed Draft Future Steps w/ Current Equipment

Current	Proposed
Zero gas cylinder standard	Zero Air supply w/ palladium
Span gas cylinder run pre & post audit	Span gas cylinder only @ pre audit
Precision cylinder for calibration purposes	Not Used
CO analyzer zero @ pre audit only	CO analyzer zero @ every point < 1.0 ppm
Regression correction w/ pre & post zero/span/precision	No regression – re zero @ all low audit points

Reason - Sufficient doubt about blend purity and/or analyzer linearity

Proposed Draft Future Steps w/ Current Equipment

Current	Proposed
Zero gas cylinder standard	Zero Air supply w/ palladium
Span gas cylinder run pre & post audit	Span gas cylinder only @ pre audit
Precision cylinder for calibration purposes	Not Used
CO analyzer zero @ pre audit only	CO analyzer zero @ every point < 1.0 ppm
Regression correction w/ pre & post zero/span/precision	No regression – re zero @ all low audit points

Reason – This corrects for zero drift at each point independently.

Reason - Pd scrubbers w/ zero air supply eliminates the need for changing cylinders to run a zero point.

Rezeroing is a 10 minute exercise. The 1.0 ppm threshold may be revised if future studies indicate.

Proposed Draft Future Steps w/ Current Equipment

Current	Proposed
Zero gas cylinder standard	Zero Air supply w/ palladium
Span gas cylinder run pre & post audit	Span gas cylinder only @ pre audit
Precision cylinder for calibration purposes	Not Used
CO analyzer zero @ pre audit only	CO analyzer zero @ every point < 1.0 ppm
Regression correction w/ pre & post zero/span/precision	No regression – re-zero @ all low audit points

Reason – Linear regression applies the same correction @ all audit points, even though drift is more severe at the end of the audit than at the beginning.

Re-zeroing the CO analyzer for points < 1.0 ppm CO, addresses the drift issue at each point, at the time of sampling.

Proposed Draft Future Steps w/ Future Equipment

- Mass flow control based audits instead of CO analyzer based audits for trace levels

  Reason - Experience has shown accuracy <u>of ± 2% of reading</u>, over repeated days and under adverse conditions (heat/humidity).

  Reason – CO analyzers vary from one unit to the next, with some having acceptable drift characteristics, and others being unacceptable

- Accurate & portable flow measuring devices for pre and/ or post audit flow measurement cost $5000/TTP setup.

- Portable flow measuring device software collects meta data for QA oversight of flow verifications.

- EPA Regional laboratories w/ flow standards equipment can verify GPT and flow measuring device accuracy annually. Flow measuring devices can also be certified annually by the manufacturer.

- The use of a mass flow controller based system will result in the use of less cylinder gases and associated analyzers, with increased accuracy.